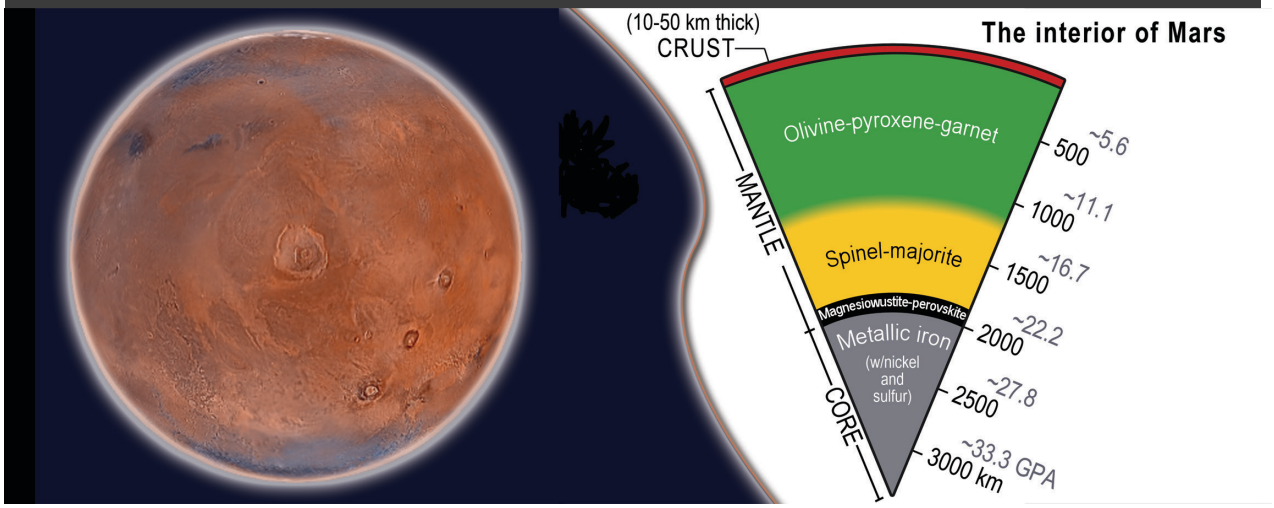
The Mantle of Mars:
Insights from Theory, Geophysics, High-Pressure Studies, and Meteorites



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The Mantle of Mars:
Insights from Theory, Geophysics, High-Pressure Studies, and Meteorites

October 10–12, 2012 • Houston, Texas

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Preface

This volume contains abstracts that have been accepted for presentation at the workshop on Mantle of Mars: Insights from Theory, Geophysics, High-Pressure Studies, and Meteorites, September 10–12, 2012, Houston, Texas.

Administration and publications support for this meeting were provided by the staff of the Meeting and Publication Services Department at the Lunar and Planetary Institute.

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Space and Earth Crystal Chemistry and Mineralogy Impact in Future Research and Innovation 21 Century **[#6006]**
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Charles Shearer

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Chairs: Bruce Banerdt
Walter Kiefer

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BREAK [15 minutes]

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Tuesday, September 11, 2012
TEMPORAL AND GEOCHEMICAL EVOLUTION OF THE MANTLE AND CRUST
1:30 p.m. Lecture Hall

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Chairs: Charles Shearer
Lars Borg

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BREAK [15 minutes]

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What Do Radiogenic Isotopes in Shergottites and Nakhlites Tell Us About the Martian Mantle? **[#6011]**
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Jones J. H. * [Contributed 15-minute talk]
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The Redox State of the Mars Mantle as Inferred from Martian Meteorites: Relationship to Volatile Content and Other Geochemical Parameters **[#6036]**
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Shearer C. K. * Aaron P. Burger P. V. Bell A. Guan Y. Papike J. J. [Contributed 15-minute talk]
Exploring the Martian Mantle Through the Micro-Scale Examination of the Geochemical, fO_2, and Kinetic Crystallization History of Olivine in Shergottites **[#6033]**
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Wednesday, September 12, 2012
HIGH-PRESSURE STUDIES OF THE MARTIAN MANTLE
8:30 a.m. Lecture Hall

High-pressure studies of melting and phase equilibria help to constrain models for the evolution of the martian mantle

Chairs: Yingwei Fei
Kevin Righter

Dasgupta R. * [Invited 20-minute talk]
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Filiberto J. * Dasgupta R. [Contributed 15-minute talk]
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Collinet M. * Médard E. Vander Auwera J. Charlier B. [Contributed 15-minute talk]
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BREAK [15 minutes]

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Righter K. * Humayun M. [Contributed 15-minute talk]
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Wednesday, September 12, 2012
CRYSTAL CHEMISTRY AND MINERALOGY
1:30 p.m. Lecture Hall

To better constrain the mineralogy and crystal chemistry of the martian mantle

Chairs: James Papike
Dave Beaty

Poulet F. * Ody A. Carter J. [Contributed 15-minute talk]
Identification and Mapping of Olivine, Anorthosite and SNC-Like Materials on Mars: Insights to Mantle Reservoirs **[#6004]**
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Draper D. S. * [Invited 20-minute talk]
Review of the Role of Garnet in the Martian Mantle **[#6015]**
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Papike J. J. * Burger P. V. Shearer C. K. [Invited 20-minute talk]
Experimental Martian Eclogite: REE Crystal Chemistry Using a Spiked QUE 94201 Composition **[#6002]**
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Peslier A. H. * [Contributed 15-minute talk]
Water in Pyroxene and Olivine from Martian Meteorites **[#6008]**
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BREAK [15 minutes]

McCubbin F. M. Elardo S. M. * [Invited 20-minute talk]
Possible Volatile Containing Phases in the Lower Crust and Upper Mantle of Mars: Inferences from Martian Meteorites and Experimental Petrology **[#6022]**
We review the volatile-bearing mineralogy of the martian meteorites and of the petrologic experiments on martian rock compositions. We use this information to speculate about volatile-bearing minerals in the lower crust and upper mantle of Mars.

Irving A. J. * [Contributed 15-minute talk]
Constraints on the Mineralogy of Mantle Source Regions of Primary Shergottite Magmas **[#6021]**
Inversion of bulk compositions of primitive shergottite liquids suggests that the three major types of mantle sources contain $Fa_{13–15}$ olivine. The mantles of Mars and Earth may have similar Mg/(Mg + Fe), but differ significantly in Ca and Al.

Righter K. * Danielson L. R. Pando K. Morris R. V. Graff T. G. Agresti D. G. Martin A. M. Sutton S. Newville M. Lanzirotti A. [Contributed 15-minute talk]

Redox Systematics of Martian Magmas with Implications for Magnetite Stability **[#6039]**

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Ding S. D. * Dasgupta R. D. [Contributed 15-minute talk]

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PRINT-ONLY PRESENTATIONS

Herd C. D. K.

Constraints on Mars Mantle Redox Conditions from Studies of Martian Meteorites: A Review **[#6030]**

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Kochemasov G. G.

Martian Mantle: Its Chemistry Repeats a Tendency of the Dichotomous Martian Crust **[#6005]**

The composition of the martian mantle can be estimated by the basalt fragment analyses made by Vikings, Pathfinder, and Spirit. Approaching southern highlands (equator) from the north, basalts become richer in Mg/Fe, Al, alkalis thus lighter than Fe-basalts.

Ruedas T. Tackley P. J. Solomon S. C.

Thermal and Compositional Evolution of the Martian Mantle **[#6009]**

This work presents combined numerical models of convection, mineralogical composition, and thermodynamical properties of the martian mantle over the past 4 Gy and predictions of various geophysical and geochemical observables derived from them.

Szurgot M.

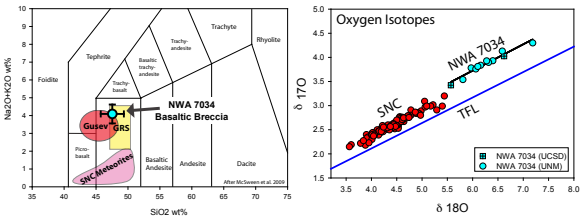
Heat Capacity of Mars **[#6001]**

Specific heat capacity, and heat capacities of Mars and the martian mantle, core, and crust have been estimated.

HETEROGENEOUS MARS: EVIDENCE FROM NEW UNIQUE MARTIAN METEORITE NWA 7034

C. B. Agee[1], [1]Institute of Meteoritics and Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131.

NWA 7034 is a new unique water-rich basaltic breccia from the early Amazonian epoch (~2.1 Ga) on Mars [1,2]. It shares some petrologic and geochemical characterisitics with known martian (SNC) meteorites, but also possesses some unique characteristics that excludes it from the current SNC grouping. The NWA 7034 meteorite is a geochemically enriched crustal rock bearing a striking compositional and average martian crust measured by recent NASA rover and orbiter missions (see figure 1).



The oxygen isotopes of NWA 7034 are also anomalous relative to SNC meteorites (figure 2). Furthermore, there are no other known achondrites or planetary samples with oxygen isotope values similar to NWA 7034, most achondrite groups have negative $\Delta^{17}O$ values or near-zero values as do rocks from the Earth and Moon -- the oxygen isotope composition of Venus and Mercury are currently unknown. There may be several possible explanations for the relatively high oxygen isotope values of NWA 7034. One possibility is that two or more distinct oxygen isotope reservoirs exist on Mars [3,4] – for example a reservoir represented by the SNC meteorites and another martian reservoir with higher $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ that we see present in NWA 7034. Earlier studies have shown that water in SNC has different $\Delta^{17}O$ values than the bulk solid, and we also observe this in NWA 7034. Thus there is already strong evidence for multiple distinct martian oxygen reservoirs, and NWA 7034 is first Mars sample showing that reservoir multiplicity extends to silicates and crustal rocks. Existence of a heterogeneous martian crust with multiple petrologic and isotopic reservoirs argues in favor of diverse mantle source regions and a mantle that is perhaps poorly mixed - calling into question magma ocean scenarios for early Mars.

References: [1] Agee C.B. et al. (2012) 43rd *LPSC* Abstract #2690. [2] Agee C.B. et al. (2012) 75th *MetSoc XXVII,* Abstract #5391. [3] Karlsson, H.R. et al. (1992) *Science* 255, 1409-1411. [4] Farquar, J. et al. (1998) *Science* 280, 1580-1582.

CONSTRAINTS ON THE COMPOSITION AND EVOLUTION OF THE MARTIAN MANTLE FROM THE ISOTOPIC SYSTEMATICS OF BASALTIC METEORITES. L. Borg[1], S. Symes[2], N. Marks[1], A. Gaffney[1], and C. Shearer[3] [1]Lawrence Livermore National Laboratory, 7000 East Ave L-231, Livermore CA, 94550, USA (borg5@llnl.gov); [2]University of Tennessee-Chattanooga, Chattanooga, TN 37403, USA. [3]University of New Mexico, Albuquerque, New Mexico 87131

Introduction: Martian basaltic meteorites (shergottites) are clearly derived from the martian mantle. Nevertheless, it is likely that they have had some interaction with crustal materials on their ascent to the surface. Therefore, in order to investigate the geochemical evolution of the martian mantle, parameters that are minimally affected by crustal interactions must be considered. Below we discuss some of the characteristics of the shergottites that can be used to constrain reservoirs and processes in the mantle. We will focus on incompatible-element ratios and isotopic compositions of samples with high Mg/Fe ratios. These element ratios and isotopic compositions are not strongly influenced by interactions with the crust, and samples with elevated Mg/Fe ratios are likely to be in equilibrium or near equilibrium with the mantle.

Relevant characteristics of basaltic meteorites: The compositional variability of the shergottite suite has been well documented [e.g. 1-2]. In summary, the shergottites have a range of compositions defined by two end-members with intermediate compositions falling on simple mixing lines between the end-members. The first end-member, usually termed "depleted" is characterized by low LREE/HREE ratios (light REE element depleted patterns), unradiogenic initial Sr isotopic compositions, and very radiogenic Nd isotopic compositions. These samples are characterized by large positive ^{142}Nd isotopic anomalies of +0.8 to +0.9 epsilon units. The REE and isotopic systematics indicate that these samples are derived from an ancient source that is highly depleted in incompatible elements. The other end-member is characterized by higher LREE/HREE ratios (flat to slightly enriched REE element patterns), highly radiogenic initial Sr isotopic compositions, and moderately unradiogenic Nd isotopic compositions. These samples are characterized by small negative ^{142}Nd isotopic anomalies of -0.2 epsilon units. The REE and isotopic systematics indicate that these samples are also derived from an ancient source, but one that is moderately to highly enriched in incompatible elements. It is important to note that several individual samples from each end-member have high Mg/Fe ratios, and in some cases, have been argued to represent near primary mantle melts [3]. This indicates that the REE and isotopic systematics of the shergottites originates in the martian mantle. There are no correlations between these parameters and Mg/Fe of the bulk rock, minerals, or other crystallization indices, indicating that differences in REE, Sr, and Nd isotopic compositions in the shergottite suite are not produced by differentiation of primary magmas in the crust [4]. Thus, these parameters likely constrain the composition, geochemical variability, and age of martian mantle source regions.

Age of mantle source regions: The Rb-Sr and Sm-Nd isotopic systematics of the martian basalts define mixing lines. Interestingly, the ages derived from both isotopic systems are concordant, suggesting these ages record a geologic event. Using the Rb-Sr systematics alone, [5] argued that this event was differentiation of the silicate portion of Mars at ~4.5 Ga. The ^{142}Nd-^{143}Nd mixing line refines this age to 4525±24 Ma [2]. However, the fact that the clinopyroxene cumulates (nakhlites) do not lie on the ^{142}Nd-^{143}Nd mixing line makes interpretation of the Sr and Nd isotopic systematics in a global context more difficult. Interpretation of the isotopic systematics of the martian meteorites is further complicated by the observation that the nakhlites and shergottites have vastly different ^{182}W isotopic anomalies ranging from approximately +0.6 in the shergottites to +3.0 in the nakhlites [6]. This clearly demonstrates that the two groups of meteorites are derived from ancient, but separate sources. The most conservative interpretation of the ^{142}Nd-^{143}Nd mixing line is therefore that it represents the age of source formation of the shergottites. It is not unreasonable to expect these samples to be closely related given the similarity in their crystallization ages and the simple mixing relationships they demonstrate [1-2, 4,5].

Interpretation of the ^{182}W data is less certain. Because Hf-W are partitioned most efficiently between metals (W) and silicates (Hf), one possible explanation is that variation in ^{182}W reflects temporally distinct interactions of the shergottite and nakhlite mantle source regions with the core. If so, it implies that martian mantle is isotopically heterogeneous and that core formation extracted W unevenly from the primordial mantle. In any case, core formation was very early in solar system history occurring around 4550 Ma [6].

Scenario of shergottite genesis: Symes [4] proposed a scenario for the origin and evolution of the depleted shergottites. Preliminary investigations completed on the enriched shergottites appear to demonstrate that this model is consistent with their petrogenisis as well [7-8]. In this scenario, the basic isotopic and REE systematics of the shergottites are inherited from depleted and highly enriched mantle sources. The enriched source is envisioned to be similar to lunar ur-KREEP and formed as the last crystallization product of the martian magma ocean. Enriched shergottites with high Mg/Fe ratios (e.g., NWA 1068) are prime examples of a product of this type of interaction. Variable bulk rock Mg/Fe, mineral compositions, and mineral types observed in the samples reflect fractional crystallization of mantle derived melts as they traverse the mantle or within magma chambers in the crust. It is important to keep in mind that the models will a tolerate small amount of open system behavior provided the fundamental REE and isotopic systematics of the shergottites remain intact. Thus, crystallization may be accompanied by small amounts of assimilation. This may be particularly relevant for highly volatile components (e.g. water) in the martian magmas.

References: [1] Borg et al. (2005) *GCA* **69,** 5819-30, [2] Borg et al., (2003) *GCA* **67,** 3519-36; [3] Norris & Herd (2006) LPSC 37 #1797; [4] Symes et al. (2008) *GCA* **17**, 1696-1710; [5] Shih et al. (1982) *GCA* **46,** 2323-44; [6] Foley et al. (2005) *GCA* **69,** 4557-71; [7] Borg et al. (2008) LPSC 39 # 1851; [8] Marks et al. (2010) LPSC 41 #2064. This work was performed under the auspices of the US DOE by LLNL under contr. W-7405-Eng-48.

HOW AND WHEN DID THE MARS MANTLE ACQUIRE HIGHLY SIDEROPHILE ELEMENTS? A. D. Brandon[1], I.S. Puchtel[2], and R.J. Walker[3], [1]Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX, 77204, abrandon@uh.edu, [2]Department of Geology, University of Maryland, College Park MD, 20742.

Introduction: Two models are presently favored to explain the highly siderophile element abundances (HSE: including Os, Ir, Ru, Pt, Pd, Re) in terrestrial planet mantles during their formation and early evolution. In the first model, HSE are extracted into iron-rich cores leaving the silicate mantles strongly depleted in these elements. In this model, the mantle HSE abundances are controlled by the partitioning behavior between metal and silicate at variable pressures and temperatures within the terrestrial bodies during core extraction. This model has been questioned because the generally chondritic HSE ratios and higher than expected relative HSE abundances in the Earth's mantle are not consistent with being derived solely from equilibrium core extraction [1,2,3]. In the second model, after core extraction sequesters more than 99% of the HSE present in terrestrial planets, their silicate mantles are then reseeded with HSE via late accretion of up to 1% by mass of chronditic material [1,2,3]. This model has been questioned because the timing of late accretion and the mechanism that will homogenously mix in the accreted material are not well understood. To examine this issue further, a suite of 23 Mars shergottite meteorites, spanning their known range in bulk composition, Rb-Sr, Sm-Nd, and Lu-Hf isotope variations were measured for ^{187}Re-^{187}Os isotopic systematics and HSE abundances [4]. The advantage of examining Mars for this issue is twofold. First, Mars is 10.7% in mass relative to the mass of Earth. Because HSE metal/silicate partitioning strongly changes with pressure [2,5], the lower pressures in the Mars mantle relative to the Earth's mantle during core extraction should have resulted in disctinct HSE abundances in their respective mantle and hence a direct comparison of the estimates of the HSE budget for each is a test for the core extraction model. Second, the martian mantle did not completely remix and homogenize after early differentation (e.g. [6]), and hence, a record of the timing of when the HSE budget was set in Mars is likely preserved.

Results and Discussion: The shergottites show a strong correlation between the initial ε^{143}Nd and γ^{187}Os in shergottites from approximately +40 and 0 to -7 and +15, respectively [4]. These relationships can be assessed in models for mixing depleted mantle-derived melts with ancient crust, and with assimilation-fractional crystallization. These models show that the correlation is unlikely to be the result of the participation of martian crust. More likely, the Os-Nd isotope correlation relates to mixing between depleted and enriched reservoirs that formed from a martian magma ocean at *ca*. 4.5 Ga. These models indicate that the shergottite endmember sources were generated by mixing between residual melts and cumulates that formed at variable stages during solidification of a magma ocean [4,7]. If so, then the HSE budget for the martian mantle was set between the time of Mars formation by ≤10 Ma after the onset of solar system condesation and the solidification of a global magma ocean in the first 100 Ma of planet history [4].

The expanded database for the HSE abundances in shergottites suggests that their martian mantle sources have indistinguishable HSE abundances to the Earth's mantle, consistent with other studies [3,8,9]. The relatively high HSE abundances in both planetary mantles likely cannot be accounted for by high pressure-temperature metal-silicate partitioning at the bases of their magma oceans, as has been suggested for Earth. This is particulary poignant given the strong differences in metal/silicate parition coefficients versus pressure for HSE and the fact that Earth and Mars must have had integrated core extraction at strongly different pressures given their strong differences in size. This relationship would instead predict strongly different estimated HSE abundances for their two respective mantles which is not observed.

Conclusions: The new and comprehensive HSE database for shergottites do not support core extraction as an explantion for their estimated abundances in the martian mantle as they are too large. Hence an alternative explanation is that HSE were instead supplied by late accretion. The late accretion must have occurred prior to the crystallization of the last martian magma ocean and thus within the first 100 Ma of solar system history in order to lock in the systematics between lithophile and Os isotopes observed for shergottites [4]. If heavy bombardment of material continued past this time onto Mars, it was not mixed into the interior.

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IMPACT OF ANELASTICITY ON MARS' DISSIPATIVE PROPERTIES – APPLICATION TO THE *INSIGHT* MISSION. J. C. Castillo-Rogez[1] and W. B. Banerdt[1], [1]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA, Contact: Julie.C.Castillo@jpl.nasa.gov.

Introduction: We revisit the interpretation of Mars' dissipation factor inferred from the secular acceleration of Phobos. The low value of that parameter has been interpreted as evidence for the existence of a highly dissipative region within Mars' mantle or crust.

While previous approaches have relied on the assumption that Mars' mantle behavior can be described by a viscoelastic model [e.g., 1], we demonstrate that material anelasticity is likely responsible for the observed dissipation, consistently with experimental measurements, and deemphasize the need for a highly dissipative region.

Modeling Approach: Material attenuation is a complex phenomenon determined by the density, geometry, and mobility of defects in the material [e.g., 2]. Per analogy with Earth, Mars' mantle deformation is believed to deform in the dislocation creep regime, and this even at the low stress exerted by Phobos. Attenuation measurements of silicate materials deformed in that regime at a forcing period of a few hours [e.g., 3] are consistent with the general description of the Andrade model. That model associates a Maxwell element representing material viscoelasticity and a term describing material anelasticity, as a function of a parameter α that represents the degree of heterogeneity of the material and β, a function of the density of defects in the material [4].

We model the interior of Mars following the approach considered in previous studies [e.g., 5] assuming that the primary source of dissipation stems from the mantle. The contribution of the elastic crust to the global dissipation budget of the planet is negligible.

Results and Discussion: In the case of the Maxwell model, the observed k_2^{pho}/Q^{pho} matches a mantle viscosity of ~$2\text{x}10^{16}$ Pa s (Fig. 1). If one accounts for the attenuation due to anelasticity, then the mantle viscosity required to explain k_2^{pho}/Q^{pho} ranges from 10^{18} to 10^{22} Pa s. The uncertainty is due to the broad range of values for the parameter α considered in this study. Indirect constraints on the value of that parameter suggest it is closer to 0.15-0.2 [2]. That lower bound corresponds to a mean mantle viscosity of 10^{22} Pa s, which in turn suggests an average mantle temperature of ~1700 K [6] and is consistent with geophysical evolution models [e.g., 7]. In the continuation of this work we will compute the attenuation spectrum of Mars for a broad range of input parameters and in the prospect of the SEIS and RISE experiments proposed as part of the *InSight* mission (under review).

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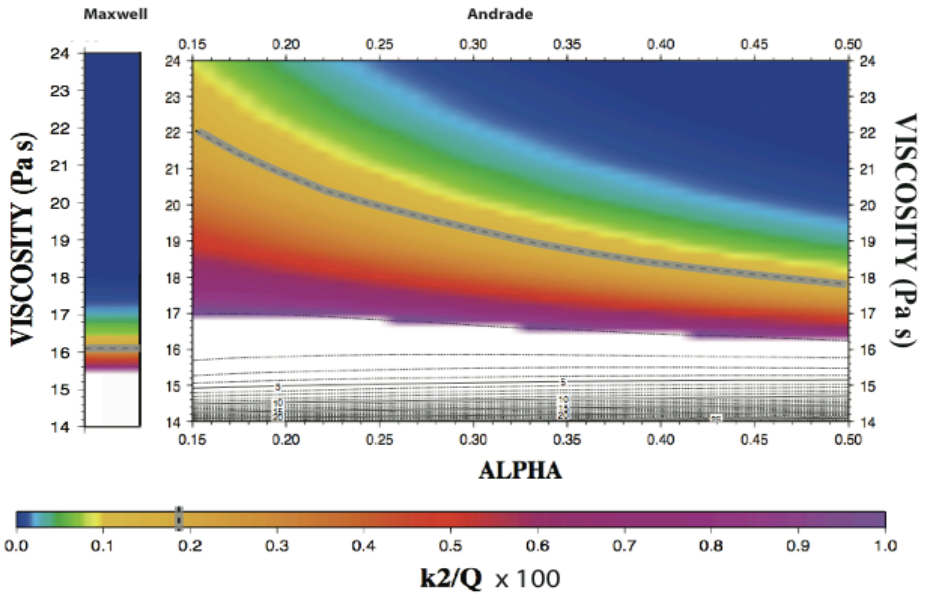

Figure 1. k_2^{pho}/Q^{pho} computed for two dissipation models, Maxwell and Andrade, as a function of the viscosity assumed for Mars' mantle and the Andrade parameter α. This model includes a core radius of 1700 km, an inner solid core of 1100 km, and a crust thickness of 50 km, consistently with the observed moment of inertia [8]. The space of results matching the observed k_2^{pho}/Q^{pho} is marked by the thick dotted line.

MARS INTERNAL STRUCTURE DERIVED FROM MGS MAGNETIC DATA. F. Civet and P. Tarits, IUEM/UEB, UMR6538 (place Nicolas Copernic, 29280, PLOUZANE, francois.civet@univ-brest.fr).

Introduction: We developed a new method to infer planetary internal electrical conductivity using global electromagnetic induction theory from satellite magnetic data. The method was tested on synthetic data calculated for the ESA SWARM mission, then successfully validated on the magnetic data from the Danish ØRSTED mission [1]. . We analyzed 8 years of magnetic data during mapping phase of Mars Global Surveyor (MGS). In contrast with Earth exospheric field, Mars has a heterogeneous external source field both in space and time. Furthermore MGS magnetic time series are not continuous which makes any standard spectral method used on Earth fail. Hence we developed a new method including a source field proxy to complete the gapped data. Two proxies of different origins, representatives of the external source time variations were calculated. The first one is derived from the MGS data. The second is obtained from Advanced Composition Explorer (ACE) data which measured magnetic characteristics of the solar wind close to the Earth during the mission period of MGS. We applied a time shift along the arm of a pseudo Parker's spiral passing through ACE position to Mars position.

Data analysis and results: We used the Martian crustal anomaly field calculated from [2] to subtract the static field. The proxy of the external variability was introduced to complete the time series to compute its spectra. We binned the data onto a grid to expand the field in spherical harmonics (SHE). This operation resulted into a time series, for which we computed the spectra in a period range from 1 day to some tens of days. The SHE was carried out on the field spectra. For each SH degree and order we separated the field into its internal and external parts and we obtained the corresponding magnetic potential. The ratio of these potentials (internal/external) is a direct function of the in-depth conductivity.

The SHE external field shows a dominant coefficient of degree 2 and order 0 which could be due to a ionic precipitation at high latitude [3]. Moreover, the energy of the internal SH coefficients appeared distributed homogeneously over the 3 degree of the SH expansion. This results is controversial because the signal is barely above the noise level. If confirmed, it could reveal a lateral heterogeneity of the mantle electrical conductivity distribution

We used a 1-D inversion algorithm that could combine the external potentials, all periods and all time windows of the MGS time series to derive 1-D electrical conductivity models. We obtained 1-D models (Fig.1) for several length of MGS time windows, from 125 days up to 210 days using both MGS and ACE proxies. All the models showed an increase of electrical conductivity from depth from about 200-1000 km, with a rapid increase between 1100 and 1300 km in depth. A sensitivity analysis on the conductivity values showed that data constrained the models up to 0.3 log unit between 0 and 1400 km depth. Below that depth, the values are not constrained by the data. The comparison of our models to mineral physics predictions for different mantle composition and temperature profiles [4], [5] suggests that the mineralogical model from [5] is a possible model for the Martian mantle mineralogy and adiabat.

Below 200 km, we observed a conductive layer in models obtain using the MGS proxy only. More test are necessary to determine whether or not this feature is an artifact or real. This result could have important implication on the composition of the crust.

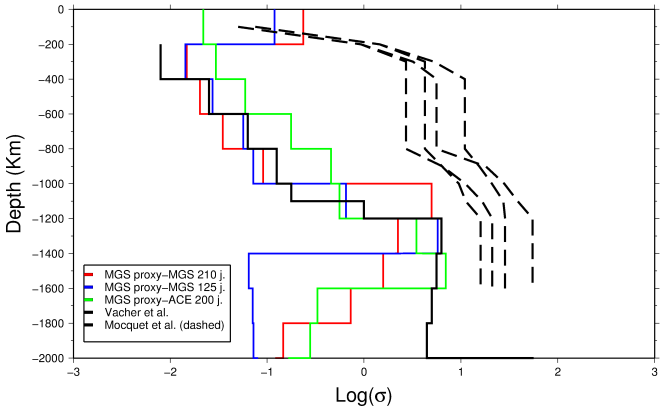

Figure 1: Electrical conductivity models (in Log scale in function of the depth) obtained for the 2 proxys: proxy-ACE (green) for a time windows of 200 days, proxy-MGS for time windows of 210 (red) and 125 (blue) days. Models from [4] (black line) and [6] (black dashed) are also shown.

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ANHYDROUS MELTING OF A PRIMITIVE MARTIAN MANTLE: NEW EXPERIMENTS AT 1-2 GPA.

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Introduction: The surface of Mars is mainly covered by basalts that were produced during partial melting of the planet interior. Model compositions of the bulk silicate Mars have been proposed based on physical constraints and correlations between element ratios from Martian meteorites and chondrites [*e.g.* 1, 2]. Such models should represent the primitive Martian mantle from which surface basalts are derived. Here, we use an experimental forward approach on a Mars mantle composition to understand the diversity of the Martian basaltic magmatism.

We have performed new melting experiments from a synthetic equivalent of [1], the most largely accepted Martian mantle model. Other reasonable models give very similar compositions [2], and share key differences with the terrestrial mantle: low Mg#, high incompatible (Na, K, P) and compatible (Cr, Mn) volatile elements. Our experiments cover the P-T conditions previously investigated by [3] (1.5 GPa, 1300-1550 °C) and have been extended to 1 and 2 GPa. Recent development of melt extraction techniques allow a better characterization of experimental melts, particularly melts produced by low degrees of partial melting. Our experimental liquid compositions are compared to Martian basalts interpreted as possible primary magmas (*i.e.* unmodified after extraction from the source region; [4, 5]). Using these compositions and previous experimental studies [3, 6], the source region of basalts present on the Martian surface can be discussed.

Experimental techniques: Experiments were performed in a piston-cylinder apparatus at 1.0, 1.5 and 2.0 GPa. This pressure range covers plausible depths of melting (80-170 km) of the Martian mantle [4, 5]. Runs were equilibrated at temperature from 1200 to 1500 °C corresponding to degrees of melting between 5 and 40 %. The starting material was synthesized from oxide and silicate powders, and loaded in Pt-Graphite capsules. These capsules were then heated at 400°C for 12h before being welded shut in order to ensure anhydrous conditions. A layer of vitreous carbon spheres was added to extract the liquid and avoid quench modifications [7].

Results and discussion: For most major elements, our experiments extend the trends previously observed by [3]. An important exception is the higher SiO_2 content of our liquids (~ 51-53% at 1.0 GPa) for low degrees of melting compared to sandwich experiments of [3] (~ 46%). Predictions made using the pMELTS model [8] are also less rich in SiO_2 (~ 46-47%). For low degrees of melting, SiO_2 rich anhydrous basalts probably results from the high alkali content of the primitive Martian mantle used in our experiments [1] compared to the Earth mantle [*e.g.* 9]. Alkalis depolymerize silicate liquids by increasing the number of non-bridging oxygen in SiO_4 tetrahedra. This decreases the activity coefficient of silica that is compensated by an increase of the SiO_2 concentration in the liquid [10].

The Adirondack class basalts and the picritic enriched (LAR 06319 and NWA 1068) and depleted (Y 980459 and NWA 5789) shergottites represent possible primary Martian basalts [*e.g.* 5]. Slight compositional variations observed between these Martian basalts and our experimental liquids are used to discuss the diversity of mantle sources. The low Si content of Adirondack class basalts compared to our experimental liquids might require the presence of a depleted source region poorer in alkalis than the primitive mantle. The CaO/Al_2O_3 ratio of shergottites (~1.2) is higher than the ones of Adirondack class basalts and experimental liquids (~0.8). Shergottites were probably derived from a mantle source depleted in Al compared to the primitive mantle and the source of Adirondack class basalts.

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IS MARTIAN MANTLE TOO REDUCED TO ALLOW CARBONATED SILICATE MELT GENERATION? R. Dasgupta[1], [1]Rice University, Department of Earth Science, 6100 Main Street, MS 126, Houston, TX 77005, USA. Rajdeep.Dasgupta@rice.edu

Introduction: Partial melting of silicate mantles is the single most important process by which terrestrial planets continue to chemically differentiate. The presence of carbon in the form of carbonates in the mantle have significant impact on this melting processs, both in affecting the depth and extent of melting [e.g., 1-3] and in modifying the major and trace element chemistry of the generated magma [e.g, 4-6]. Experiments and natural observations on terrestrial rocks and analogs over the past four decades have established that the role of carbonated melting of the Earth's upper mantle is critical in understanding the compositional range of basalts on our planet and flux of incompatible elements and volatiles from the interior. But the question remains whether such framework of carbonated manle melting is applicable to sister planet Mars. Furthermore, does the chemistry of Martian basalts call for carbonated melting in the mantle of Mars and if yes, can the estimated conditions of Martian mantle be reconciled with generation of carbonated magmas?

The Role of Oxygen Fugacity: One of the most critical parameters that affect the stability of carbon in the form of carbonates at high-temperature mantle rocks (an assemblage of olivine + opx + cpx + garnet) is oxygen fugacity, fO_2. The stability of carbon in the form of CO_2-rich fluids or carbonates relies on the two well-established buffer reactions [7, 8] –

$2C + O_2 = 2CO$; $C + O_2 = CO_2$ (CCO) (1)

$MgSiO_3+MgCO_3 = Mg_2SiO_4+C+O_2$ (EMOG/D) (2)

These reactions suggest that CO_2-rich fluids or mineral carbonates (such as dolomite and magnesite solid solution; XCO_2 ~0.5) can coexist, in equilibrium with graphite/diamond, with Earth's upper mantle rocks at fO_2 as low as ~1.6 log units below the FMQ buffer. At fO_2 lower than such, graphite/diamond becomes stable. However, this fO_2 limit of carbonate stability does not take into account the effect of dilution of CO_2/carbonate component (XCO_2<0.5) that may be plausible, if the phase of interest is a melt rather than crystalline carbonate. Recent experimental work [9] allows fO_2 estimates in diamond/graphite and carbonated melt bearing mantle assemblages with the knowledge melt CO_2 content. Application of such calibration to new and existing experiments on partial melting of carbonated peridotite from our group and from literature suggests that a carbonated silicate melt with CO_2 content as high as ~5 wt.% can be stable in equilibrium with graphite at logfO_2 ~FMQ-3.2 and at pressures ≥2 GPa.

Generation of Carbonated Melt in the Martian Mantle?: fO_2 estimated from SNC meteorites suggests that Martian basalts span a range of 4-5 log units, log-fO_2 ~FMQ-4.5 to FMQ [e.g., 10-12], potentially reflecting similar range for their mantle sources. However, if fO_2 estimates of only primitive (e.g., Y980459) and isotopically depleted samples are considered to be relevant for most of the mantle, then logfO_2 becomes restricted to FMQ-4.5 to FMQ-2.5 [e.g., 10, 11]. Because this range of fO_2 is distinctly lower those imposed by the CCO and/or EMOG/D buffers at magmatically relevant depths, recent studies [e.g., 13] suggested that carbon storage in the Martian mantle occurs in the form of graphite/diamond and a strongly carbonated melt (such as strongly alkalic basalt or carbonatite) generation is not likely. Although this may be the case for some domains, complete absence of carbonated melt stability in the Martian mantle may be potentially at odds with distinctly alkalic, silica-undersaturated basalts such as Wishstone class of rocks, which can be explained by carbonated melting [14]. The estimated fO_2 condition of graphite-present, carbonated silicate melt stability as stated above, however, suggests that carbonated silicate melt with ~5 wt.% CO_2 can be stable at fairly reduced condition, not too dissimilar from the fO_2 estimated from primitive Martian meterorites. Therefore, future studies will need to consider carbon-present redox melting of the Martian mantle, which generates low-degree carbonated silicate melt potentially primary to some of the Gusev crater basalts.

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WHAT DO RADIOGENIC ISOTOPES IN SHERGOTTITES AND NAKHLITES TELL US ABOUT THE MARTIAN MANTLE? V. Debaille[1] and A. D. Brandon[2], [1]Laboratoire G-Time, Université Libre de Bruxelles, Av. F.D. Roosevelt, CP160/02, 1050 Brussels, Belgium (vinciane.debaille@ulb.ac.be), [2]Department of Earth and Atmospheric Sciences, University of Houston, Houston TX 77204, USA for second author (abrandon@uh.edu).

Introduction: The SNC suite (shergottites, nakhlites and chassignites) provides the only samples we can directly analyze for understanding the martian interior. Unfortunately, they are differentiated lavas and do not directly reflect the composition of the martian mantle. On the other hand, radiogenic isotope ratios are not fractionated during magmatic processes and can decipher not only the composition but also the time-integrated evolution of the source of these martian samples. In order to understand the evolution of the martian mantle, $^{142}Nd/^{144}Nd$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ isotope ratios have been measured in several nakhlites and shergottites, then providing a consistent story for the evolution of Mars.

Martian mantle mineralogy: The shergottites have Lu/Hf and Sm/Nd ratios that define a well correlated trend [1]. This relationship has been interpreted as mixing between a depleted and an enriched reservoir [2-7]. The depleted reservoir has been directly related to depleted shergottites [1, 2]. It is postulated to have a Sm/Nd ratio that is lower compared to the lavas themselves, and using a Monte-Carlo simulation, the mineralogy of the source of depleted shergottites has been modeled by 60% olivine, 21% clinopyroxene, 9% orthopyroxene and 10% garnet [1]. Such a mineralogical assemblage corresponds to the upper martian mantle at a depth of 250-400 km [8]. The origin of the enriched reservoir has often been related to the martian crust. However, the Re-Os systematics in shergottites preclude this hypothesis [4, 9]. In contrast, it has been proposed that this enriched reservoir is located at the top of the martian mantle and is broadly similar to the lunar KREEP source, where it is composed of quenched residual melts resulting from 98-99% of the crystallization of a magma ocean [1, 10].

Crystallization of the martian magma ocean and its fate: Crystallization of a magma ocean is a bottom-up process that is expected to form refractory Mg-rich cumulates first, and Fe-rich cumulates at the end of the process, at the top of the mantle [11]. It has been shown that depleted shergottite mantle source crystallized ~22 million years (Myr) after solar system formation (assf) (using the recently revised decay constant of ^{146}Sm [12]) with the same mineralogical assemblage as above [1]. The enriched source crystallized later, around ~83 Myr assf [7]. At the end of the crystallization of the magma ocean, one can expect to observe a density gradient that can be re-equilibrated via a mantle overturn [11]. It has thus been proposed that nakhlites provide the first geochemical evidence of the occurrence of a mantle overturn, because of the decoupling between their $\varepsilon^{142}Nd$ and $\varepsilon^{182}W$ systematics [13]. Both nakhlites and depleted shergottites show recent sources (~1.3 Gyr ago for nakhlites, ~450 Myr ago for depleted shergottites) in the martian mantle that are directly inherited from the crystallization of the martian magma ocean and its subsequent overturn. This observation is even more critical when considering ALH84001 that is 4.09 Gyr old and that has geochemical affinities to more recent shergottites [10]. This implies that the martian mantle preserved ancient geochemical signatures related to early differentiation.

Preserving an unmixed martian mantle over Mars history?: A major paradox of the martian mantle is thus how to preserve the chemical heterogeneity observed in SNCs despite a martian mantle expected to be convective at the present time [14]. Mantle convection should rapidly homogenize chemical heterogeneities. As such, some have proposed that the martian mantle has stopped convecting a long time ago [15]. A numerical model recently developed [16] shows that a convective mantle can still be poorly-mixed in the case of stagnant-lid tectonic regime. This is the case of Mars, showing a stagnant lid for at least the last 4 Gyr [17].

Conclusions: The isotopic signatures of shergottites and nakhlites provide a consistent picture of the martian mantle, from the formation of Mars and the crystallization of a magma ocean, followed by mantle overturn, to the more recent times when their mantle sources melted to produce these igneous rocks. A convective but still poorly-mixed mantle can be explained by the martian plate tectonics, characterized by stagnant-lid regime.

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SULFUR CONCENTRATION OF MARTIAN MAGMAS AT SULFIDE SATURATION AS A FUNCTION OF DEPTH S. Ding[1] and R.Dasgupta[1], [1]Department of Earth Science, Rice University, 6100 Main Street, MS 126, Houston, TX 77005, USA.sd35@rice.edu.

Introduction: Deep planetary sulfur cycle is one of the most important geochemical cycles for the differentiation processes and ancient climate of Mars. Sulfur is thought to be the dominant light element in the Martian core [1] while SO_2 and H_2S are proposed to exert a strong greenhouse effect required to maintain liquid water on Martian surface in the past [2]. In order to constrain the fate of sulfur during early differentiation of Mars, i.e., magma ocean crystallization and early mantle melting and crust formation, it is critical to know how much sulfur could be dissolved in the Martian magma. Martian basalts are thought to be more sulfur rich than the terrestrial basalts because the former have higher FeO contents (17-20 wt.% in shergottites, [3]), which in turn can dissolve more S^{2-} in the melt. However, most experiments constraining sulfur concentration at sulfide saturation (SCSS) are conducted on FeO poor terrestrial basalts (5.2-12 wt.% FeO, [e.g., 4]) and recent experiments on Mars-relevant, high-FeO basalts are restricted to <1 GPa [5].

Methods: We simulated basalt-sulfide equilibria using an end-loaded piston cylinder apparatus, half-inch $BaCO_3$ assembly, and graphite capsule at 1600 °C and at each pressure of 1.0, 1.5, 2.0, and 2.5 GPa. Two synthetic starting compositions,similar to Martian meteorites Yamato980459 (Y98) and NWA 2990 (NWA), which are thought to represent primary Martian magmas [6], were used. A third silicate composition equivalent of Y98+1.4 wt.% H_2O was used to constrain the effect of water on Martian magma SCSS. Experiments were conducted with 85-70 wt.% silicate + 15-30 wt.% FeS mixtures. Texture and phase compositions were investigated using a Cameca SX50 electron microprobe. Raman spectroscopy was employed to determine the oxidation state of sulfur dissolved in the melt.

Results: All experiments produced two immiscible, silicate and sulfide, quenched melts. Experiments with NWA resulted in glassy silicates and those with Y98 produced melts with dendritic crystals. Sulfide saturation was confirmed by the presence of 20-500µm diameter blobs of quenched sulfide liquid embedded in the silicate melts.Tiny specs of sulfides (<0.5µm) were also present in all experiments, dispersed throughout the melt, regardless of run duration. These latter sulfide specs were, therefore, regarded as an exsolved phase during quench and were included in SCSS. Fe-S bonding in glassy silicates was recognized from the~420 cm^{-1}[7] peak in Raman spectra.

Measured SCSS for all the studied compositions decreases with increasing pressure and increases with water content.Y98+1.4wt.% H_2O has the highest SCSS, with S content varying from 5440 to 4380 ppm from 1 to 2GPa. SCSS for NWA varies from 5400 to 3700 ppm and for Y98 from 4800 to 3500 ppm from 1 to 2.5 GPa. Compared to previous studies on FeO-poor terrestrial compositions, SCSS of Martian compositions are higher by >1800 ppm at similar pressures and temperatures. A positive correlation between SCSS and FeO contents in the melt was observed. SCSS in this study agreed well with the prediction of SCSS by the empirical model derived from lower pressure (1 bar and 0.8 GPa) experiments on Martian basalts [5].

Discussion: Most shergottites have 1300-2700 ppm S [8] and primitive shergottitic magma and Martian mantle equilibration is thought to take place at average pressure-temperature of ~1.0-1.5GPa and ~1365-1525°C [6]. If the shergottites were sulfide-saturated at the final conditions of melt-mantle equilibration, primary shergottites are expected to have ~4000-4500 ppm S. Our results in combination with bulk S contents of natural shergottites thus imply that a large amount of sulfur (~2200-3200 ppm) might have degassed during ascent of Martian basalts.

Extrapolating our measured SCSS, using an exponential function, to the base of the Martian magma ocean (14 GPa [9]) yields an SCSS of 349-384 ppm. At this depth if all the sulfur was dissolved in the silicate magma ocean, $D_S^{metal/sil}$ could be constrained ≥260 for 10-16 wt.% S in the metallic core [1].

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REVIEW OF THE ROLE OF GARNET IN THE MARTIAN MANTLE. D. S. Draper, Astromaterials Research & Exploration Science Directorate, NASA Johnson Space Center, Houston, Texas; david.draper@nasa.gov.

Introduction: All basaltic martian meteorites have superchondritic CaO/Al_2O_3, ranging from ~1.0-1.7 compared to ~0.8 for chondrites. If bulk Mars is essentially chondritic, martian basalt source rocks were depleted in primordial Al by up to 60% [1], possibly from early garnet (gt) crystallization in a martian magma ocean (MMO) [2, 3] (although martian basalt source regions are not gt-bearing [4]). Early-formed gt would raise CaO/Al_2O_3 in residual liquids; later crystallization of olivine and pyroxene should leave this ratio relatively unperturbed [5-8]. But gt undergoes important compositional changes with pressure that may constrain the minimum depth of the initial MMO.

Effect of pressure on gt composition: The pressure-induced transition of gt to majorite (maj) increases Si from the canonical 3.0 atoms per formula unit (pfu) and decreases Al from the canonical 2.0 pfu. For gt in Mg-rich systems (Mg# ~90), the maj shift is fairly abrupt, and occurs at ~15 GPa. In contrast, Al pfu in more Fe-rich lunar and chondritic compositions (Mg# ~80, e.g. [9]) drops more gradually. This change in Al content will in turn affect CaO/Al_2O_3 of liquids residual to early gt removal in a MMO. The more gradual change in Al pfu with pressure helps constrain the depth at which initial gt removal took place.

Effect of maj content on CaO/Al_2O_3: More majoritic gt requires a larger percent crystallization to produce a liquid of a given CaO/Al_2O_3, as summarized in Fig. 1. Ranges are shown for all the shergottites (~1.1-1.7, grey box), and for their calculated parent liquids [10-15] (~1.05-1.3, blue box). The virtually identical values (~1.2) for QUE94201 and Yamato 980459, thought to represent liquid compositions [16, 17], are denoted by the narrow red band; the green band is the chondritic value. Black curves represent loci of CaO/Al_2O_3 in liquids remaining after removal of gt having a particular Al content with the fraction crystallized denoted on each curve. For example, a residual liquid with CaO/Al_2O_3 of 1.2 will be produced by 5% crystallization of gt having ~1.65 Al pfu, or by 7% crystallization of gt with 1.25 Al pfu, and so forth.

CaO/Al_2O_3 of martian basalt source regions: Within the range of CaO/Al_2O_3 values for martian basaltic meteorites, the value of ~1.2 for QUE and Y98, thought to represent liquids rather than crystal accumlates, is particularly significant. These two compositions occupy opposite ends of the spectrum of martian basalt compositions, with Y98 being the most primitive and QUE one of the most evolved. Their identical CaO/Al_2O_3 suggests that this value is a signature of early gt crystallization and reflects that of the upper-mantle source for martian basalts. We can thus evaluate the range of gt maj contents, and hence pressures, over which this signature was imparted.

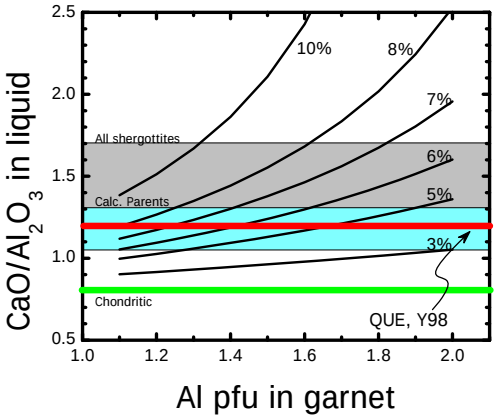

Figure 1. CaO/Al_2O_3 of liquids remaining after removal of gt having range of maj contents. Curves labeled with percent gt removed. See text for discussion.

Magma ocean depth constraints. To estimate pressures of MMO early gt formation, Al pfu contents that produce liquids having CaO/Al_2O_3 ~1.2 can be matched with the ranges in that parameter with pressure described above. Doing so implies that the minimum pressure of early gt crystallization is ~9-10 GPa (~900 km depth) with ~5% crystallization of gt having ~1.65 Al pfu, and a maximum of ~20 GPa (~1500 km) with 7-8% crystallization of gt having ~1.15 Al pfu. These depths probably do not correspond to the base of the magma ocean, however. Vigorous convection could lead to an inertial zone capable of suspending early-formed crystals (as suggested for the Moon by Spera [18]). Even deeper crystallization could occur in which γ-olivine is an important early phase [6], but it would not perturb the chondritic CaO/Al_2O_3. The depths inferred here are thus minimum estimates. Calculated REE contents of residual liquids after early gt fractionation using our predictive models [19, 20] indicate that the best-fit conditions are in about the middle of the range outlined here, at ~15 GPa with 6-7% crystallization of gt having Al pfu = 1.2-1.4.

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CONSTRAINTS ON THE DEPTHS AND THERMAL VIGOR OF BASALT FORMATION IN THE MARTIAN MANTLE. J. Filiberto[1] and R. Dasgupta[2], [1]Southern Illinois University, Filiberto@siu.edu, [2]Rice University, Rajdeep.Dasgupta@rice.edu.

Introduction: Until recently, the SNC meteorites represented the only source of information about martian igneous chemistry [1]. This changed with the Mars Exploration Rovers, which have analyzed basalts on the surface of Mars in Gusev Crater and Meridiani Planum [2, 3]. Compared to the Martian meteorite basalts, the basalts in Gusev Crater are thought to be much older (~3.65 vs. 1.0-0.17 Ga) [4, 5] and have distinctly different chemistries [6]. Because of the differences in basalt chemistry, we can constrain how the Martian mantle may have changed through time.

Pressure-Temperature Estimates of Martian Basalt Genesis: *Inverse Experimental Modeling Approach:* Near-liquidus phase relations can show whether or not a basalt could be a primitive mantle derived liquid [7]. This approach has been applied to the Martian basalts: meteorites Yamato 980459 [8] and NWA 1068 [9] and to the Adirondack-class basalt Humphrey analyzed on Mars at Gusev Crater [10, 11] and the Home Plate-class pyroclastic basalt Fastball [12].

Geochemical Modeling Approach: To estimate the pressures and temperatures of formation of calculated primary magmas, we can also use olivine-melt Mg-exchange thermometry [13, 14] and silica activity in the melt barometry [14]. This approach has been applied to the Martian surface basalts in Gusev Crater and Bounce Rock in Meridiani Panum [15].

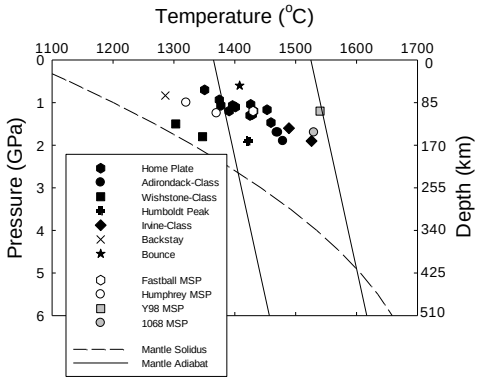

Figure 1. Temperatures and pressures calculated for primitive magma compositions for basalts from Gusev Crater and Meridiani Planum [15]. Experimental results for the olivine-orthopyroxene multiple saturation pressure for Fastball, Humphrey, Yamato 980459 (Y98) and NWA 1068 are shown [8-12]. Also shown for reference, by the dashed line, is the solidus of Martian mantle and, by solid line, the mantle adiabat [15].

Results: Figure 1 shows the estimates of pressures and temperatures of basalt genesis for surface basalts and meteorites based on the experimental and geochemical modeling results. The experimental results for meteorite Yamato 980459 show a multiple saturation of the melt with olivine and a low-calcium pyroxene at 1.2 GPa and 1540 ± 10 °C [8], suggesting that the meteorite represents a primary melt that separated from its mantle source at a depth of ~100 km. The geochemical modeling results [15] for surface basalts from Gusev Crater show a range in pressure-temperature of formation from 1-2 GPa and 1300-1525°C consistent with experimental results on the Home Plate basalt Fastball [12]. Bounce Rock in Meridiani planum shows a P-T of formation of 0.6 GPa and 1410°C.

Implications: The Gusev Basalts and Bounce Rock are both thought to be Noachian in age (4.5-3.6 Ga) based on geomorphology and crater counting [5, 16] and give the same range in mantle potential temperatures (1445 ± 80 °C and 1475 ± 15 °C [15]) and initial melting pressures (2.7-5 GPa and 4.0-4.6 GPa [15]); yet, these basalts were analyzed in different locations on the surface. This suggests that the average mantle potential temperature calculated (1450 ± 80 °C) for these basalts may represent a global average for the Martian mantle during the Noachian. If we compare our estimate of ancient Martian mantle potential temperature with the terrestrial mantle potential temperatures based on Archean komatiites [≥ 1700°C; [17]], we observe that the Martian mantle was actually significantly colder than the terrestrial mantle.

The younger (472 ± 47 Ma for Y98; [18]) Martian meteorites suggest a hotter mantle potential temperature [8]. However, they may not represent a global estimate for the basaltic magmas on Mars and instead they may represent localized thermal anomalies [8, 14] similar to thermal anomalies (beneath ocean islands such as Hawaii) in the Earth [e.g., 13]. Future studies documenting basaltic compositions from relatively younger Martian surface of known locations will be necessary to evaluate secular cooling of the whole Martian mantle through time.

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Constraints on Mars Mantle Redox Conditions from Studies of Martian Meteorites: A Review. C. D. K. Herd, Department of Earth and Atmospheric Sciences, 1-26 Earth Sciences Building, University of Alberta, Edmonton, AB, T6G 2E3, Canada, herd@ualberta.ca.

Introduction: All martian meteorites are derived from mafic magmas by variable degrees of accumulation. By inverting crystallization products to parental magmas, the conditions of partial melting and the compositions of their mantle sources may be inferred. All but 11 of the 61 unique (i.e., unpaired) martian meteorites are shergottites. These rocks have little to no cumulate texture and are therefore useful probes of the interior of Mars.

Several oxybarometers are applicable to planetary basalts such as the shergottites (see [1] for a review); the olivine-pyroxene-spinel and Fe-Ti oxide oxybarometers have since been updated, and are now readily available as online tools through http://ctserver.ofm-research.org/webcalculators.html.

Models of shergottite formation: A distinct characteristic of the shergottites is that they record a wide range of time-integrated incompatible element enrichment, clustering into three distinct geochemical groups based on their Rb-Sr and Sm-Nd isotopic compositions and REE patterns (depleted, intermediate, and enriched; see [2] for a recent review). Early and rapid differentiation of the silicate portion of Mars is called upon to generate enriched and depleted reservoirs by ~4.5 Ga, either through formation of primitive martian crust by partial melting of the mantle, or crystallization of a magma ocean [3-4]. In the latter model, the last dregs of magma ocean crystallization comprise the enriched portion, and the cumulate mantle is the depleted counterpart [4-5]; whether a basalt eruptive is depleted or enriched depends on the mix of depleted or enriched components in its mantle source.

A correlation between oxygen fugacity, as determined by application of oxybarometers to shergottites, and time-integrated incompatible element enrichment was recognized on the basis of a handful of shergottites [6-7]. Interpreted in the context of mantle source variation, this trend implies that the depleted, cumulate portion of the Martian mantle is reduced, near Iron-Wüstite (IW), whereas the enriched portion is oxidized, near Fayalite-Magnetite-Quartz (FMQ; equal to ~IW + 3.5 log units)[8]. As such, the oxygen fugacity of an Amazonian shergottite is strongly dependent on the redox state of its mantle source, which was set during magma ocean crystallization at ~ 4.5 Ga.

Do all shergottites follow the trend? Most shergottites follow the expected trend of increasing incompatible element enrichment (e.g., La/Yb ratio) with increasing oxygen fugacity (Figure 1). However, recent studies have shown some exceptions among the olivine-phyric shergottites. NWA 1068/1110 contains an early, megacrystic olivine+pyroxene+chromite assemblage that records an oxygen fugacity 2.5 log units below FMQ (FMQ – 2.5), whereas oxides in the groundmass record FMQ + 0.3 (Fig. 1); this difference is interpreted as representing incorporation of xenocrysts into an oxidized magma [9]. LAR 06319 shows a similar range between early and late assemblages (Fig. 1); in this case, however, the increase of ~2 log units likely occurred during fractional crystallization and ascent [10]. When estimates of the oxygen fugacity of the parental magmas to the poikilitic ("lherzolitic") shergottites are included (Fig. 1) [11], it appears that the shergottite mantle sources have a more limited range of redox state, from FMQ – 4 to FMQ – 2, and that the higher oxygen fugacities of some shergottites are a combination of mantle source characteristics and oxidation during ascent and emplacement.

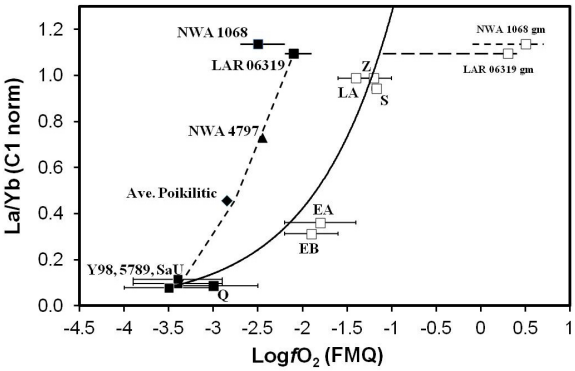

Figure 1. Summary of oxygen fugacity estimates for shergottites vs. whole rock La/Yb. Data from [8-10] and references therein. Solid line is polynomial fit to Y980459 (Y98), NWA 5789, SaU 005 (SaU), QUE 94201 (Q), EET 79001 (EA, EB), Los Angeles (LA), Shergotty (S) and Zagami (Z). Dashed line is inferred trend for mantle sources.

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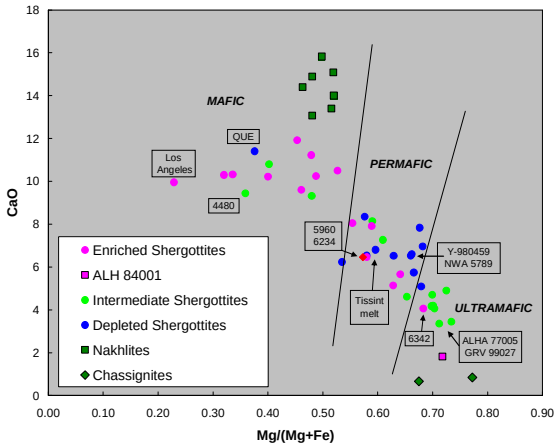
CONSTRAINTS ON THE MINERALOGY OF MANTLE SOURCE REGIONS OF PRIMARY SHERGOTTITE MAGMAS. A. J. Irving, Dept. of Earth & Space Sciences, University of Washington, Seattle, WA 98195, USA, irving@ess.washington.edu.

Introduction: Given the existence of 65 unpaired Martian meteorites, we are now in a much better position to more meaningfully assess the ranges in bulk composition of the major groups. Since all of these specimens are igneous rocks, it should be possible to constrain some aspects of the composition and mineralogy of their source regions (assuming that the effects of crystal accumulation, fractional crystallization and assimilation can be taken into account). This in turn should lead to improved models of evolution of the Martian mantle, at least for those regions producing the magmas represented by the meteorite specimens.

Magmatic Groups: At this writing the Martian specimens comprise 8 nakhlites, 2 chassignites, 54 unpaired shergottites and 1 orthopyroxenite (with shergottite affinities). Among the shergottites there are at least three distinct groups based on lithophile trace element character (E = enriched, D = depleted and I = intermediate), and within each of these there are variations in indices of fractionation from more primitive to more evolved. The textures of shergottites in each category range from aphyric (intersertal, subophitic, diabasic, microgabbroic or gabbroic) to poikilitic (P) to olivine/orthopyroxene-phyric (OP), which signify differences in cooling rate and probably depth (possibly ranging from volcanic to plutonic hypabyssal).

Bulk Compositions: Determination of representative bulk compositions of shergottites is fraught with difficulties because of heterogeneities in grain size and grain distribution. Aphyric specimens present fewer problems, but since those evidently have experienced magmatic evolution they are unsuitable for inversion to constrain primary mantle souce region characteristics. The majority of olivine-phyric shergottites have been shown to contain excess early cumulus olivine crystals (e.g., [1]), so that bulk compositions of most are more magnesian than their parent liquids. Poikilitic shergottites do not show evidence for such crystal accumulation and may well represent magmatic liquids.

From a plot of bulk ***mg*** versus CaO (Figure 1) for shergottites whose compositions have been well-analyzed from sufficiently representative sample masses or clean cutting dust, it can be seen that each of the three major trace element groups exhibit a trend from very magnesian compositions to more ferroan compositions. In Table 1 the most magnesian (i.e., most primitive) liquids for each group have been selected, and the liquidus olivine in equilibrium with them calculated using a $K_D^{olivine\text{-}melt}$ of 0.355 [2].



Specimen	*Group*	*Texture*	***mg***	*CaO*	*Fa in olivine*
NWA 6342	E	P	0.683	4.06	14.2 [obs 31]
ALHA 77005	I	P	0.712	3.35	12.5 [obs 25]
NWA 5789	D	OP	0.661	6.55	15.4 [obs 14]

For depleted shergottite NWA 5789 (and also for Yamato 980459) the predicted equilibrium olivine compositions are very close to those observed in the most magnesian macrocryst cores [3], so that these specimens may well be primary magmas from the depleted mantle source. For both the intermediate and enriched shergottites the predicted equilibrium olivine compositions are significantly more magnesian than the most magnesian olivine chadacrysts [4]. However, since ALHA 77005, GRV 99027 and NWA 6342 have poikilitic textures (signifying more prolonged and variable cooling histories), it would not be unexpected for early-formed olivine crystals to become more ferroan by progressive reaction with surrounding melts.

If the selected shergottites do indeed represent the most primitive magmatic liquids for each of the trace element groups, then the olivines in their mantle sources are predicted have compositions of $Fa_{13\text{-}15}$. This range is very similar to that inferred for olivine in terrestrial mantle sources of primitive basalts; however, the pyroxene in the shallow Martian mantle must be much lower in Ca and Al than deduced for Earth.

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RARE EARTH ELEMENT FRACTIONATIONS DURING SNC PETROGENESIS. J.H. Jones, KR, NASA/JSC, Houston, TX 77058 (john.h.jones@nasa.gov).

Apparent mixing relationships among shergottites. Most shergottites can be treated as ~recent mixing between a depleted, mantle-derived basalt and an old, enriched martian crust with high $^{87}Sr/^{86}Sr$. (EET 79001 may be an exception). The endmember compositions are: (i) $^{87}Sr/^{86}Sr = 0.69898$ (BABI); $\varepsilon(Nd) = +55$; and (ii) $^{87}Sr/^{86}Sr = 0.7375$; $\varepsilon(Nd) = -18$. In this model, the depleted shergottites have experienced 1-2 wt.% crustal contamination; the intermediate shergottites have experienced 6-8 wt. % crustal addition; and the enriched shergottites are comprised of 20-24 wt.% crust. The enriched (high $^{87}Sr/^{86}Sr$) component need not be crust, but that is our preferred model (e.g., [1]). The least contaminated shergottite is QUE 94201 (QUE) with an initial $\varepsilon(Nd) = \sim+50$. Therefore, our shergottite REE fractionation models will only be applied to QUE.

Missing melts. This simple two-component mixing model masks considerable complexity. Knowing the age of individual shergottites and their isotopic initials, it is possible to calculate the time-integrated Sm/Nd of the shergottite source regions, which are always smaller than the those of the shergottites themselves [2]. The implication of this change in Sm/Nd between the shergottite source and actual shergottites requires a missing melt phase that is LREE enriched. This is because no mantle mineral prefers LREE over HREE.

The simplest model is for small-degree partial melts to have escaped the shergottite source regions shortly before melting of the shergottites themselves. The attraction of this model is twofold: (i) At the time of shergottite genesis, there had to be sufficient heat to induce partial melting; and (ii) The amount of Sm/Nd fractionation that the missing melts induce is very large. Other models require even larger fractionations.

The complexity of shergottite petrogenesis suggests that we first attempt to model nakhlite partial melting, where the complexities of missing melts are not known to exist.

Nakhlite petrogenesis. The time-integrated $^{147}Sm/^{144}Nd$ of the nakhlite source region was ~0.235, whereas the $^{147}Sm/^{144}Nd$ of Nakhla itself is ~0.135 [3]. Therefore, large Sm/Nd fractionations are required, implying that nakhlite petrogenesis requires very small-degree partial melts (e.g., [4]).

There is not space to document the nakhlite model in entirety. However, we expect HREE in the nakhlite source should be ~2X CI abundances, and we also know that the Sm/Nd ratio of that source was 1.2X CI.

$D(REE)_{pyx/liq}$ are taken from [5]. One value of $D(Ca)_{pyx/liq}$ is chosen and then all pyroxene D(REE) $_{pyx/liq}$ are parameterized from that single value. $D(REE)_{gnt/liq}$ were modified from those of [6,7]

Except for La, all REE in the nakhlite model are within 25% of the Nakhla parent liquid of [8]. The model requires an extremely small (0.1%) partial melt that yields a melt with a $^{147}Sm/^{144}Nd$ of 0.113 and a residue having a $^{147}Sm/^{144}Nd$ of ~0.6. This compares favorably to the measured $^{147}Sm/^{144}Nd$ of nakhlite NWA 5790 glass (0.118) and other models of nakhlite genesis (e.g., [3]).

Shergottite petrogenesis. The situation is more complicated in that we do not have the LREE-enriched melts from the shergottite mantle (i.e., the missing melts). Instead, we sample melts produced from the depleted residues of those missing melts. And, once again, large REE fractionations are required.

Modeling of this is accomplished by generating a missing melt and then comparing the shape of the residual REE pattern to that of QUE, assuming that a third melting of the shergottite source region will quantitatively remove any remaining REE and produce a shergottite. The REE composition of the model QUE source region (before generation of a missing melt) is much like that of the nakhlite source except that it is slightly more depleted and has a significantly larger $^{147}Sm/^{144}Nd$ ratio (0.285 vs. 0.235 [2]).

Two very similar but slightly different solutions are presented. The first solution is best for fitting the entire REE pattern (i.e., approximately flat when normalized to QUE). The second model solution seeks only to produce the Sm/Nd fractionation that is required by that system ($^{147}Sm/^{144}Nd$ ~0.50), because the complete REE model did not ($^{147}Sm/^{144}Nd$ ~0.45). As in the case of the nakhlites, both models require very small degrees of partial melting.

And even though there appears to be much commonality between the nakhlite and shergottite models, there are also differences: (i) shergottite model has considerably less pyroxene; and (ii) the shergottite pyroxene is much less calcic than in the nakhlite model. These two differences are consistent with the more-depleted nature of the shergottite source.

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"Space & Earth Crystal chemistry & Mineralogy impact in future Research & Innovation 21 Century "

In the earth and other planet most of the element found in other word we can say that all entire the planet based on element form which occurred by ion's, element & compound. In today scenario the most of the planet innovation search to the hydrate ion presences it shows that the presences of water in the past scenario .Crystal formation also a indication the past presences in the water of Hydrate Ion's. Rocks In the historical background and modern innovation also showed that two type of weather shows Physical and Chemical we also indicate mineralogy is the branch of Physical & Chemical environment.

Physical Weathering –Physical weathering depend on the condition of the physical character mean rocks, elements, minerals but the role of minerals is so high due to the formation of crystal. In this weathering the formation of pole or joint junction .

Formation of Junction :- junction meanly a certain process of temperature and pressure condition in the different joint which occurred the erosion of rock & crust . Some time joint form free space or free air also gave the opportunity to enter the agents.
General Single theory of the formation of crystal

Physical & Chemical Weathering Factor involved
Air + Free Space in Rocks + Agents = Formation of Crystal

Physical Environment (Junction, Temperature & Heat, Pressure)

Crystal Development :- Crystal compound theory :- In this scenario the crystal single type of formed in earth Plant ,Animal and different human activity and then the Physical Chemical and bio chemical factors work to formed a crystal. After the formation of single crystal then 2 crystal attached theory depend on the formation of junction because the same way of junction formation it will occurred the early development of crystal compound theory.

The Thermochemical Evolution of the Martian Mantle: Alkali Abundances and Their Effects on the Mantle Solidus and Magma Production Rate over Time

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Studies of the martian meteorites suggest that the martian mantle is enriched in alkalis (Na and K) and iron (lower magnesium number) relative to Earth. The Mars primitive silicate mantle is estimated to have 0.5-0.9 wt% Na_2O with a magnesium number of 75-80 [1-4]. In comparison, the primitive silicate Earth mantle has Na_2O of 0.35 wt% and a magnesium number of 89 [5]. Both differences lower the solidus temperature on Mars relative to Earth.

To quantify the effects of composition on solidus temperature, we analyzed experimental melting results for a suite of peridotite melting studies at 1 and 3 GPa with Na_2O between 0.02-0.66 wt% and magnesium number between 75 and 90.5 [3, 6-13]. We calculated multivariable least squares fits to test how changes in total alkali content ($Na_2O + K_2O$) and magnesium number affect the solidus. The 3 GPa solidus varies between 1430 and 1515 °C, depending on composition. Our parameterization explains 95% of the total data variance, with an RMS misfit of 7 °C. At 1 GPa, the solidus varies between 1195 and 1270 °C. Our parameterization explains 62% of the data variance, with an RMS misfit of 15 °C.

Based on this parameterization and the differences in mantle composition summarized above, the Mars mantle solidus is about 30 °C lower than the Earth solidus at 1 GPa and about 50 °C lower at 3 GPa. At both pressures, the alkali abundance and magnesium number each account for about half of the difference in solidus temperature. Incorporating these differences in solidus temperature into a model of pressure-release mantle plume melting [14] increases plume melt production rate by a factor of 3-10. Clearly, the small differences in mantle composition between Earth and Mars are important and might be the difference between a planet that is still slightly active volcanically and a planet that is magmatically dead at present.

The differences in chemical composition cited above are for the primitive mantle prior to separation of any crust from the mantle. Because Na is incompatible, it partitions into the crust during volcanism and thus both its abundance in the mantle and its effect on the solidus temperature and the magma production rate decline over time. On the other hand, the magnesium number of the mantle does not change significantly with time, and its effect on the solidus should continue to be important to pressure release melting in mantle plumes on present-day Mars. We recently modeled the thermal and magmatic evolution of Mars using a model that accounts for water loss from the mantle and its effects on the solidus [15]. In our on-going work, the model is being adapted to also track transport of Na into the crust and to parameterize the effects of Na loss from the mantle on the solidus using the results described above.

The Gusev Crater basalts and pyroclastics measured by the MER rover Spirit have Na_2O 2-3.5 wt % , while the much younger olivine-phyric shergottites typically have $Na_2O < 1.2$ wt %. This may indicate loss of Na from the mantle over time, but differences in other factors such as melt fraction and melting pressure also need to be considered, and the two rock types may represent separate mantle reservoirs [16].

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MARTIAN MANTLE DYNAMICS CONSTRAINED BY GEOLOGICAL AND GEOPHYSICAL OBSERVATIONS S. D. King[1], P. Sekhar[1], and K. K. Cheung[1], [1]Department of Geosciences, Virginia Tech, Blacksburg, VA 24061 (sdk@vt.edu, pav06@vt.edu, kcheung@vt.edu)

A successful global model of Martian dynamics should explain: A) the rapid emplacement of the Tharsis region [1]; B) the location of Tharsis rise relative to the crustal dichotomy [2]; C) the subsequent limited volcanic activity after the formation of Tharsis rise [3]; and D) heat flow out of the core that is consistent with the absence of a present-day, internally-generated magnetic field [4]. Calculations of convection with both a thick and thin lithosphere show that an upwelling plume will arise beneath the center of the thick lithosphere [5-7]. Geological evidence is consistent with a track of volcanism originating near the South Pole and migrating toward the current location of Tharsis rise [8]. A region of thick crust follows this same track [9]. These observations are consistent with numerical calculations and tank experiments in a domain with a thick and thin lithosphere, where a plume forms beneath the thick lithosphere and migrates to the boundary of the lithosphere thickness contrast [5].

While the conceptual model described above explains many features of Tharsis rise (e.g., A and B above), the question of why Mars had such a voluminous period of volcanism early that appears to have shut down over a short period of time (C above) is not well addressed. Also sometimes lost in the discussion is the fact that while significantly less voluminous, the region around Elysium Mons may have been volcanically active until nearly the present time [3]. Thermal history calculations are formulated by balancing energy and do not solve the coupled conservation of mass, momentum, and energy as in convection calculations. While most convection calculations use an internal heat source that does not vary with time, Sekhar and King [10] explore calculations where the internal heating varies with time using the abundances of Uranium, Thorium, and Potassium in Lodders and Fegley [11]. They conclude that the decay of radiogenic elements could explain the transition from voluminous volcanism early in Mars history to the limited volcanism at present day. In fact, they found it difficult to produce present day melting–at odds with the young crater ages of some flow units in the Tharsis region [3].

While including decaying heat sources explains the rapid shutdown of melt consistent with the rapid emplacement of Tharsis rise and subsequent limited volcanic activity, we find two challenges: creating low-degree (i.e., degree-one) mantle structure; and the timing of the formation of Tharsis. We focus on low-degree structure because we recognize that while significantly less voluminous, Elysium Mons has also been volcanically active for much of Mars history [3].

The Challenge of Low- Degree Structure

The challenge of producing low-degree mantle structures (e.g., degree-one convection) arises from the assumed lithosphere structure. Many of the degree-one calculations start from a steady-state spherical axisymmetric structure expanded out to the sphere. In Sekhar and King [10], the calculations start from a uniform temperature interior with a 50 Myr old lithosphere generated using an error function solution. Roberts and Zhong [12] find low-degree structures with a viscosity increase of a factor of 8, while we require at least a factor of 25 increase.

The Challenge of Delayed Tharsis Timing

The majority of Tharsis rise was emplaced by the end of the Noachian [1,3], yet in our calculations the thermal instability near the core-mantle boundary responsible for volcanism rises to the surface within 100 Myrs of the start of the calculation. It is difficult to delay the formation of the plume to be consistent with the time between the formation of the dichotomy and the formation of Tharsis. In our calculations, Tharsis forms so early we expect it would be difficult to resolve the ages of Tharsis rise and the crustal dichotomy. The time for a plume to transit from the south pole to the present location may reconcile the age of Tharsis rise with the short time required to form an instability at the core mantle boundary.

These challenges suggest that it is worthwhile considering two volcanic mechanisms; a deep, instability to initially form Tharsis rise in the Noachian and small-scale convection to explain the smaller, long-lived volcanic activity that continues to present [13].

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MARTIAN MANTLE: ITS CHEMISTRY REPEATS A TENDENCY OF THE DICHOTOMOUS MARTIAN CRUST; Kochemasov G.G., IGEM of the Russian Academy of Sciences, 35 Staromonetny, 119017 Moscow, kochem.36@mail.ru

The comparative wave planetology [1, 2 and others] is based on this fundamental thesis: orbits make structures. It means that inertia-gravity forces arising in planetary bodies due to their movements in non-circular (elliptical, parabolic) keplerian orbits with periodically changing curvatures and accelerations produce in planetary spheres undulations. Having standing character and four directions (ortho- and diagonal) these undulations (waves) interfere forming uplifting (+), subsiding (-) and neutral compensated (0) tectonic blocks. These blocks, naturally, are regularly disposed and their sizes depend on wavelengths. The longest fundamental wave 1 (long $2\pi R$) inevitably produces tectonic dichotomy with one hemisphere rising (+) and another falling (-). The rising (continental) hemisphere increases its planetary radius. The falling (oceanic) hemisphere diminishes its planetary radius. As all planetary bodies rotate, tectonically and hypsometrically different levels blocks (hemispheres) must regulate (equilibrate) their angular momenta: otherwise a globe will tend to fall to pieces (destroy itself). As the angular velocity of rotation of all blocks in one body is the same, the equilibration must be done by play between radii and densities. The subsiding blocks thus must be denser than the uplifting blocks. Our observations confirm this: at Earth oceans are basaltic and continents are on average andesitic. Mars also obeys this law: the northern lowlands are Fe-basaltic and the southern highlands are andesitic at least at the dichotomy boundary ('Pathfinder") and must be else less dense further south (we proposed albitites, syenites and granites as candidates to these low density rocks [2]). Ratios between light and dark minerals as well as Fe/Mg in dark minerals play an important role in regulation of basaltic densities. Compositions of crustal basalts having the mantle origin are very sensitive to hypsometric (tectonic) position of planetary blocks. At Earth oceanic depressions are filled with Fe-rich tholeiites, on continents prevail comparatively Mg-rich less dense continental basalts. This tendency for martian basalts becames clear after TES experiment on MGS [3]. The TES data on mineralogy of low-albedo regions show that type 1 spectra belong to less dense basic rocks (feldspar 50%, pyroxene 25%) than type 2 spectra (feldspar 35%, pyroxene + glass 35%). It means that the highland basaltoids are less dense than the lowland ones. Mars with its sharp relief range (~6 km hypsometric difference between the northern lowlands and southern highlands) requires very sharp density difference between composing these blocks lithologies. Earlier predicted [2] alkaline lithologies for continents were found at Columbia Hills highland outlier [5].

A globular shape of rotating celestial bodies means that their tropical and extra-tropical belts have significantly different angular momenta. To level partly this inequality bodies tend to diminish radius and mass in tropics and increase them in extra-tropics. Traces of these destructive and constructive actions are fixed in planetary geospheres. The remote geologic mapping of **Mars** reveals these traces rather obviously. "Mysterious" contact zone of the martian lowlands and highlands with obvious traces of destruction expressed in widespread development of chaotic and fretted terrains is a good evidence of this. So called martian pedestal craters are broadly developed polarward of 40° N and S latitudes [4]. Usually they are considered as impact craters but more correctly they should be assigned to normal volcanic features expulsing volatile-rich silicate material (a kind of mud, thus "mud volcanoes'). An intensive volcanism through pedestal craters in extra-tropic belts should be compared with intensive plume-driven basaltic terrestrial volcanism also in extra-tropics – both are constructive events.

The mantle derived basaltic rocks of Gusev crater (near the continent) could be compared with Vikings' basalts ("open ocean"). As it should be, in Vastitas Borealis the basalts are Fe rich or Fe-basalts. They are less siliceous, have less K, Mg and Al. The Gusev crater basalts have higher Mg/Fe, AL/Ca, K_2 0 (up to 0.5%, especially in soils, comparable to 0.7% in Pathfinder andesites also in the contact). Even nepheline-normative rocks were already observed in the first analyses of the Gusev crater basalts [6]. All indicates that approaching highlands basalts become "lighter" (less dense) as it requires physics of a rotating body.

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CONSTRAINTS ON MARS MANTLE EVOLUTION FROM SM-ND AND LU-HF ISOTOPE COMPOSITIONS OF SHERGOTTITES AND ALH 84001

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Introduction: Calculated Lu-Hf and Sm-Nd initial isotope compositions of shergottites and ALH 84001 indicate a hybridized upper-mantle is a likely source of these materials. The hybridized mantle formed during crystallization of a Mars magma ocean where cumulates with depleted Sm/Nd and Lu/Hf ratios and late-stage residual liquids with enriched Sm/Nd and Lu/Hf ratios represent the depleted and enriched mantle end-member compositions, respectively [1-3].

Discussion: Shergottites span a range in source $^{176}Lu/^{177}Hf$ and $^{147}Sm/^{144}Nd$ ratios of 0.028 – 0.052 and 0.18 – 0.28, respectively. Source $^{176}Lu/^{177}Hf$ and $^{147}Sm/^{144}Nd$ compositions of ALH 84001 (ALH), calculated for the measured Lu-Hf age of 4.091 Ga, are 0.018 and 0.172, respectively [2]. Although ALH is distinct both in age and lithology, its source compositions are consistent with mixtures of depleted and enriched mantle end-member components that describe the Lu-Hf and Sm-Nd mixing array of shergottites (Figure 1). Furthermore, calculated source compositions of ALH indicate that it is derived from a source that has the highest proportion of the enriched component relative to recognized shergottites.

Modeling of a crystallizing 2000 km thick magma ocean by Debaille et al. [3,4] provides a data set of mantle reservoir Sm-Nd and Lu-Hf compositions we have tested for compatibility with the observed source variation of shergottites. An upper mantle (200 - 750 km) assemblage consisting of olivine, CPX, OPX, and garnet (with a majorite component) cumulates and trapped residual liquid in equilibrium with the cumulates [3] is consistent with the inferred depth of mantle partial melting (250 – 400 km [5]). Furthermore, mixing of the cumulates and trapped liquid in this upper-mantle assemblage can describe the Lu-Hf and Sm-Nd source characteristics of shergottites and ALH (Figure 1). This upper mantle assemblage formed during magma ocean crystallization of the remaining ~35 – 7% liquid [3]. The calculated $^{147}Sm/^{144}Nd$ and $^{176}Lu/^{177}Hf$ ratios of the very late stage residual liquid after ~ 98% magma ocean crystallization are < 0.16 and < 0.017 [3], respectively. Although the $^{176}Lu/^{177}Hf$ composition of this very late stage liquid is compatible (within uncertainty) with the model, the $^{147}Sm/^{144}Nd$ ratio is too low to be a major component of the enriched end-member [2]. In light of both enriched shergottite and ALH source data, Lu-Hf and Sm-Nd compositions of very late stage residual liquids and associated cumulates are not consistent with the enriched component of shergottites sources.

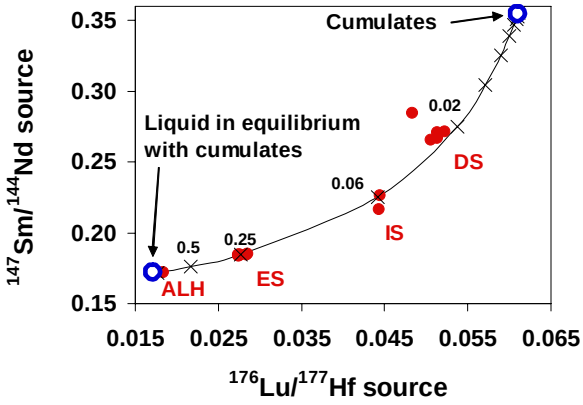

Figure 1. Mixing diagram for shergottites and ALH $^{147}Sm/^{144}Nd$ and $^{176}Lu/^{177}Hf$ source compositions. Red dots are shergottites; DS = depleted shergottites; IS – intermediate shergottites; ES = enriched shergottites; ALH = ALH 84001. The black binary mixing line is based on source compositions of cumulates and liquids in equilibrium with the cumulates in the upper mantle assemblage (UM1) of [3] produced in a 2000 – 1350 km deep MO. Isotope data used for the source calculations of shergottites come from [2-12]. Labeled mixing proportions (black symbols) are based on the fractions of residual trapped liquid.

The shergottites and ALH do not appear to sample highly incompatible element enriched source material reflective of a late stage residual liquid after >98% magma ocean crystallization [2]. If this is the case, this material was removed during impact processing or it was not uniformly distributed such that it did not develop near the volcanic centers and influence shergottite compositions.

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POSSIBLE VOLATILE CONTAINING PHASES IN THE LOWER CRUST AND UPPER MANTLE OF MARS: INFERENCES FROM MARTIAN METEORITES AND EXPERIMENTAL PETROLOGY. F. M. McCubbin and S. M. Elardo, Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131 (fmccubbi@unm.edu).

Introduction: Mars is often described as a volatile-rich planet [1-2], and these enrichments are often extended to the magmatic volatiles [3-4]. On Earth, magmatic volatiles (i.e., H_2O, F, Cl, C-species, and S-species) play an important role in the physicochemical processes that control thermal stabilities of minerals and melts, magma eruptive processes, and transportation of economically important metals. However, the abundances and roles of magmatic volatile elements may differ between Earth and Mars. In the present study we aim to review the volatile-bearing mineralogy of the martian meteorites, as well as what has been gleaned from experimental studies of volatile-bearing martian magmatic systems. We use this information to speculate as to some potential volatile-bering minerals in the lower martian crust and martian mantle.

Volatile-bearing phases in martian meteorites: Volatile-bearing mineral phases do not make up the dominant mineralogy of any martian meteorite discovered to date. In fact, the shergottites only seem to have the volatile-bearing mineral apatite [5; Figure 1, 6-7], with some reports of amphibole in mineral-hosted melt inclusions [8-9], but these have not been identified and analyzed with modern techniques. The nakhlites and chassignites have a a more diverse array of volatile-bearing mineral phases than the shergottites that includes kaersutite, Ti-biotite, apatite, chlorian ferrohornblende, and potassic chlorohastingsite [9-10, 12-16]. However, it should also be noted that the volatile-bearing silicates have only been identified in mineral-hosted melt inclusions that remained sealed throughout crystallization and cooling [12-14]. A ternary plot of F-Cl-OH components for all of the volatile-bearing minerals analyzed to date in martian rocks is presented in Figure 1.

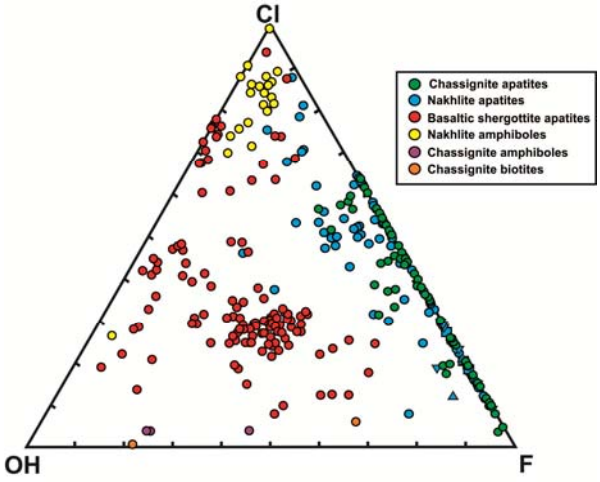

Figure 1. Ternary plots of X-site occupancy (mol%) of volatile-bearing mineral phases from chassignites, nakhlites, and basaltic shergottites. For the apatites, OH was calculated assuming 1 – F – Cl = OH. EPMA data yielding (F + Cl) > 1 atom are plotted along the OH^- free join assuming 1 - Cl = F. For the amphiboles that do not commonly have oxy-components in the O(3) site (Nakhlites), OH was not directly measured, so we assumed that 2 – F – Cl = OH, whereas Chassigny kaersutite and Ti-biotite were only plotted if OH was measured directly because of the likelihood of O^{2-} substitution in the monovalent anion site. In order to plot amphibole within the F-Cl-OH ternary, we normalized the molar sums of F, Cl, and OH from the SIMS analyses to one. Data from [5, 9-14] and unpublished data by McCubbin.

Volatile-bearing phases in petrologic experiments: The phase relations of a number of martian compositions have been conducted with the addition of magmatic volatile components [3, 17-23]. Of these experiments, only three studies have investigated the liquid-line-of-descent to the point of volatile-bearing mineral saturation [18, 20, 23]. Similar to what has been observed in the martian meteorites, amphibole and apatite are the primary volatile-bearing phases that formed. The modal abundance of amphibole in the experiments was typically much higher than observed in any of the martian rocks, indicating that martian magmas either had a smaller volatile load than the experiments or martian magmas underwent substantial degassing on the way to the surface. Biotite has not yet been experimentally produced directly from a martian composition. Apatite compositions become increasingly Cl-rich with increasing pressure, but at the pressures of the crust mantle boundary on Mars, apatite highly prefers F over Cl and OH^- [23].

Discussion: Based on estimates of mantle volatile abundances and mineral stability, apatite and perhaps amphibole could be stable in the lower crust and mantle of Mars. Graphite has also been proposed to reside in the martian mantle [24], and this is consistent with recent reports of macromolecular carbon in mineral-hosted inclusions in the shergottites [25]. More work is needed to place any real constraints on this topic.

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MARS MANTLE CONVECTION: INFLUENCE OF PHASE TRANSITIONS ON CORE ACTIVITY. Nathalie C. Michel[1], Olivier Forni[2,3] and Steven A. Hauck, II[1] . [1]Dept. of Earth, Environmental, and Planetary Sciences, Case Western Reserve University, Cleveland, OH 44106 (nathalie.michel@case.edu); [2]Université de Toulouse; UPS-Observatoire Midi-Pyrénées; IRAP; Toulouse, France; [3]CNRS; Institut de Recherche en Astrophysique et Planétologie; 9 Avenue du Colonel Roche, BP 44346, 31028 Toulouse Cedex 4, France.

Introduction: Altough Mars currently has no global dynamo-driven magnetic field, crustal remnant magnetization [1] indicates that Mars had a global magnetic field early in its history with an active core dynamo [2]. Early work suggests that the dynamo was active for a few hundred million years [3,4] and ceased during the early Noachian. However, it has also been suggested that magnetic field may have briefly reappeared after its first disappearance [5]. More recently, [6] found inconsistencies with the magnetic signatures recorded over younger and smaller impact and younger structures that challenge thinking on the magnetic field timeline of Mars and place the cessation at ~3.8 Ga.

The presence of mineralogical phase transitions in the Martian mantle has been recognized to play an important role in the style of mantle convection [e.g., 7], and the dynamo of the planet [8]. While the exothermic phase transitions tend to accelerate mantle flow and influence volcanic evolution, the endothermic spinel to perovskite phase transition tends to inhibit convection [9] and induces layered convection [10]. Increasing in depth due to mantle cooling, the spinel to perovskite phase transition may disappear and be responsible for a reactivation of a core dynamo [5].

Model: To analyze the effects of phase transitions in the mantle and the consequences on the planet's thermal evolution, we have employed the axisymmetric, spherical shell, mantle convection code CITCOM [11] extended to account for secular cooling of the core [12]. We consider five cases (Figure 1) with varying core sizes, between 1360 km to 1700 km [8, 13-18].

Results: Due to the secular cooling of the core, CMB temperatures, and hence core heat flux, generally decrease with time. Eventually, the heat flux falls below the critical value required to sustain a core dynamo. An increase in the core heat flux is observed in models with a small (SC) or a large core (LC) but only when the activation energy is very low . Our simulations demonstrate that this sudden increase of the heat flux is not necessarily attributable to the displacement of an endothermic phase transition, but solely depends on the onset of convection in the mantle, which increases the efficiency of planetary cooling.

Conclusion: Our simulations demonstrate that it is difficult to rejuvenate a dynamo, even when a perovskite layer occurs in planet with a small core. However, disapperance of an endothermic phase transition is not necessarily the only mechanism able to increase the core heat flux as it depends rather on the time when convection begins. Indeed, in models with a low activation energy and a cold initial mantle, a core dynamo reactivation as suggested by [5], or even a late core dynamo cessation as in [6], are possible.

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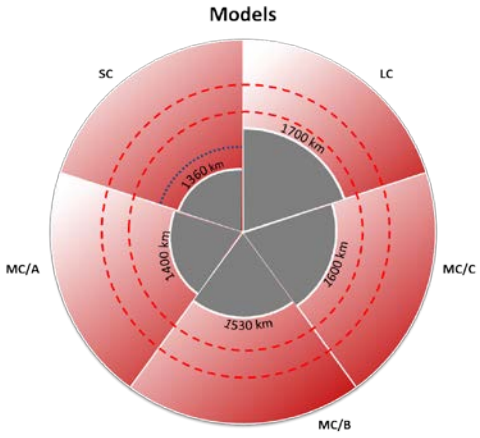

Figure 1. Schematic view of the models studied. The core is indicated in gray. The blue dotted line indicates the position of the endothermic phase transition while the red dashed lines are the locations of the exothermic phase transitions. See [12] for a detailed description.

MARTIAN IGNEOUS GEOCHEMISTRY: THE NATURE OF THE MARTIAN MANTLE. D. W. Mittlefehldt[1], L. T. Elkins-Tanton[2], Z. X. Peng[3] and J. S. Herrin[3*], [1]Astromaterials Research Office, NASA/Johnson Space Center, Houston, TX 77058, USA (davd.w.mitlefehldt@nasa.gov), [2]Dept. of Terrestrial Magnetism, Carnegie Institution for Science, Washington, DC 20015, USA, [3]Sample Analysis Research Dept., Engineering and Science Contract Group, Houston, TX 77058, USA, **Presently:* School of Materials Science and Engineering, and Earth Observatory of Singapore, Nanyang Technological University, Singapore 639798.

Introduction: Mafic igneous rocks probe the interiors of their parent objects, reflecting the compositions and mineralogies of their source regions, and the magmatic processes that engendered them. Incompatible trace element contents of mafic igneous rocks are widely used to constrain the petrologic evolution of planets. We focus on incompatible element ratios of martian meteorites to constrain the petrologic evolution of Mars in the context of magma ocean/cumulate overturn models [1]. Most martian meteorites contain some cumulus grains, but regardless, their incompatible element ratios are close to those of their parent magmas. Martian meteorites form two main petrologic/age groupings; a 1.3 Ga group composed of clinopyroxenites (nakhlites) and dunites (chassignites), and a <1 Ga group composed of basalts and lherzolites (shergottites).

Incompatible Element Considerations: A spider diagram shows that martian basalts and clinopyroxenites have mirror incompatible element patterns (Fig. 1) [*cf.* 2]. Depleted basalt QUE 94201 has positive anomalies in P, Sr and the high field strength elements (HFSE) Zr and Hf, but not in the HFSE Nb, Ta, Th or U. Depleted basalt NWA 5789 has only small positive anomalies in Zr and Hf. NWA 5789 and QUE 94201 are magma compositions [6, 7], and their incompatible element patterns approximate those of their source regions. The clinopyroxenite Nakhla has negative anomalies in P, Zr and Hf, but no Sr anomaly.

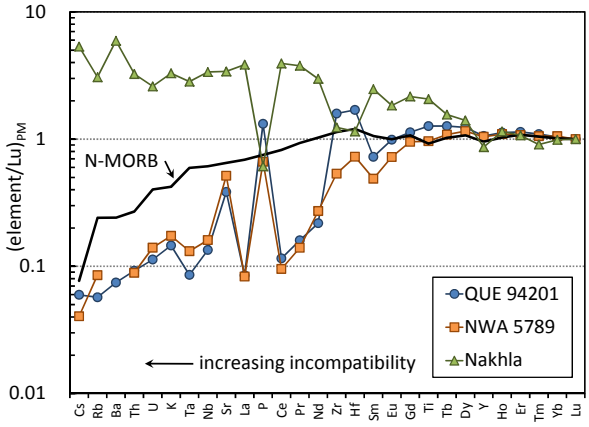

Figure 1. Arachnophilic diagram of select martian meteorites compared to terrestrial N-MORB [3], normalized to primitive mantle compositions [4, 5].

Magma Ocean Considerations: Trace element and isotopic considerations require that depleted basalts were derived from cumulates formed during a magma ocean stage on Mars [8, 9]. Coupled anomalies in P, Sr, Zr and Hf (Fig. 1) suggest that these elements are dominated by a common phase. Majorite garnet was suggested to be the phase responsible for anomalous P behavior [9]. The majorite/melt K_d for P is ~1 for Earth-relevant compositions at appropriate pressures [10], but K_ds for Zr and Hf are much less [11], suggesting that the anomalies in P, Zr and Hf may not have resulted solely from majorite accumulation.

The lowermost mantle is predicted to contain Mg-silicate perovskite [12]. This phase has Zr and Hf K_ds >1, but its P and Sr K_ds are less than unity [13]. Thus, while accumulation of Mg-silicate perovskite may have caused the Zr and Hf anomalies, it cannot also explain the P and Sr anomalies.

Martian clinopyroxenites were also derived from light REE-depleted sources [*e.g.* 14], consistent with majorite garnet accumulation. Zirconium and Hf abundances suggest that the clinopyroxenite source region accumulated later (and higher), possibly after cessation of Mg-silicate perovskite crystallization.

We will run magma ocean models incorporating trace element partition coefficients à la [1] to test the hypotheses for the generation of trace element anomalies discussed here, constrained to match growth of radiogenic isotope ratios.

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EXPERIMENTAL MARTIAN ECLOGITE: REE CRYSTAL CHEMISTRY USING A SPIKED QUE94201 COMPOSITION. J.J. Papike (jpapike@unm.edu)[1], P.V. Burger[1], and C.K. Shearer.[1] [1]Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, 87131.

Introduction: This abstract represents the start of a campaign to "map" the upper mantle of Mars using high pressure studies on martian meteorite compositions which represent liquids or near liquids. Our first experiments focus upon mineralogical and crystal chemical aspects of the basalt-eclogite transformation on Mars. It is anticipated that like Earth, eclogites are not the dominant upper mantle assemblage. However, like Earth they may be important hosts for P, Cl, F, OH, Ti, REE, Sr, Y, high-field-strength elements, Hf, and Zr in the upper mantle. This initial experimental study evaluates the major and trace element crystal chemistry of potential martian eclogite assemblages using a martian melt composition (QUE 94201).

Analytical Approach: The starting composition for this study is similar to that of the QUE 94201 meteorite, but "spiked" with total rare earth elements (REE), V, Sc = 5.5 oxide wt.%. The high spike levels allowed for the measurement of the REEs in garnet and omphacite by ion probe (secondary ion mass spectrometry; SIMS) and electron microprobe (EPMA). High pressure (4GPa) experiments were conducted in a Walker-style multi-anvil press at the Institute of Meteoritics at the University of New Mexico using the procedure, cell assembly, and calibrations described by Agee et al. [1]. EPMA analyses were conducted using the JEOL JXA 8200 electron microprobe in the Institute of Meteoritics and Department of Earth and Planetary Sciences at the University of New Mexico. SIMS analyses of the REE (La, Ce, Nd, Sm, Eu, Dy, Er and Yb) were collected on the Cameca 4f instrument at the Institute of Meteoritics at the University of New Mexico.

Results and Discussion: The 4 GPa spiked QUE charge resulted in eclogite after 4 hours run time in a multi-anvil press. The mode is garnet=49 vol.%, omphacite=32 vol.%, coesite=10 vol.%, and mesostasis=8 vol.%. The garnet has a compositional ranges from $Al_{69.4}Gr+An_{21.0}Py_{9.6}$ to $Al_{41.5}Gr+An_{28.1}Py_{30.4}$ to $Al_{40.3}Gr+An_{22.6}Py_{37.1}$ (where Al = almandine, Gr +An = grossular + andradite, and Py = Pyrope). Pyroxene has a jadeite and acmite component of up to 26.0 and 9.9%, respectively. The garnet is enriched in REE over omphacite (Fig. 1); this is especially true for the HREE. The prime substitution couple that incorporates REE into garnet is: $REE^{3+}{}_{X\ Site} + Mg^{2+}{}_{Y\ Site} \leftrightarrow R^{2+}{}_{X\ Site} + Al^{3+}{}_{Y\ Site}$, where R^{2+}= Ca, Mn^{2+}, Fe^{2+}, Mg . This is a very effective couple that accounts for both charge balance and ionic size restrictions in individual sites. The prime substitution couple that incorporates REE into omphacite is: $REE^{3+}{}_{M2\ Site} + Na^{+}{}_{M2\ Site}$ for 2 $Ca^{2+}{}_{M2\ Site}$. This is a less effective couple than that for garnet because Na is pulled in two directions in omphacite; it must balance the Al in the M1 site in the jadeite component and it also has to provide a charge deficiency for each REE^{3+} cation in the M2 site . REE patterns (normalized to bulk charge) for garnet, omphacite and mesostasis are presented in Fig. 1. The calculated REE pattern for the mesostasis is based on mass balance consideration of total spike level of REE, the modal abundance of phases, and REE SIMS analyses of garnet and omphacite. The mesostasis (+phosphates) estimate provides closure for the total REE budget. Whereas pyroxene and garnet are LREE depleted, the estimated phosphate is LREE enriched. It appears that the LREE liberated by the breakdown of plagioclase with increased pressure primarily resides in the mesostasis. The garnet is enriched in REE relative to omphacite. This is especially true for the HREE.

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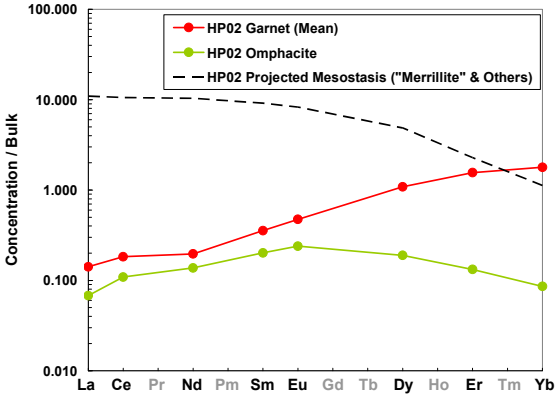

Figure 1. SIMS analyses of high pressure, (REE) spiked experiment.

WATER IN PYROXENE AND OLIVINE FROM MARTIAN METEORITES. A. H. Peslier[1,2], [1]Jacobs Technology, ESCG, Mail code JE23, P. O. Box 58447 Houston, TX 77258-8447, USA. anne.h.peslier@nasa.gov, [2]ARES, NASA-Johnson Space Center, Houston. TX 77058, USA.

Introduction: Water in the interior of terrestrial planets can be dissolved in fluids or melts and hydrous phases, but can also be locked as protons attached to structural oxygen in lattice defects in 'nominally' anhydrous minerals (NAM) like olivine, pyroxene, or feldspar [1-3]. Although these minerals contain only tens to hundreds of ppm H_2O, this "water" can amount to at least one ocean in mass when added at planetary scales because of the modal dominance of NAM in the mantle and crust [4]. Moreover these trace amounts of water can have drastic effects on melting temperature, rheology, electrical and heat conductivity, and seismic wave attenuation [5]. There is presently a debate on how much water is present in the martian mantle. Secondary ionization mass spectrometry (SIMS) studies of NAM [6], amphiboles and glass in melt inclusions [7-10], and apatites [11, 12] from Martian meteorites report finding as much water as in the same phases from Earth's igneous rocks. Most martian hydrous minerals, however, generally have the relevant sites filled with Cl and F instead of H [13, 14], and experiments using Cl [15] in parent melts can reproduce Martian basalt compositions as well as those with water [16]. Martian meteorite minerals are in the process of being analyzed by Fourier transform infrared spectrometry (FTIR) in order to constrain the role of water in this planet's formation and magmatic evolution.

Results and discussion: Analysis of two pyroxene grains from nakhlite MIL 03346 yield a minimum of 1.6 ppm H_2O in each grain while one pyroxene grain from nakhlite NWA 998 contains about 4 ppm H_2O (Figure). These water contents are at least 100 times lower than those found in most terrestrial pyroxenes [3]. No water could be detected in an olivine from NWA 998. Nakhlites are thought to represent the cumulate part of thick lava flows [17]. The augitic pyroxene is their main phase and crystallized first from the parental magma [18, 19]. However, melts may have circulated through the cumulate pile and reacted with it. In that respect MIL 03346 represents the least re-equilibrated of the nakhlites while NWA 998 is the most compositionally transformed by this process [18, 19]. The water contents of a melt in equilibrium with the pyroxenes can be calculated using the partition coefficient ($D_H^{px/melt}$) equation of [20]. A melt in equilibrium with MIL 03346 pyroxene would contain 200 ppm H_2O. If this value represents the water content of the parent melt, then the martian mantle produces relatively dry magmas compared to that of Earth (for example melt inclusions in olivines from primitive MORBs contain 1200 ppm H_2O [21]). Given that H is incompatible during crystallization, the higher water content of NWA 998 pyroxene may reflect re-equilibration for water with percolating more evolved melts containing at least 400 ppm H_2O. This scenario would be consistent with 619-1100 ppm H_2O that have been measured in NWA 998 apatite [11], one of the last phase to crystallize. A melt in equilibrium with these apatites would contain ≥ 2800 ppm H_2O using a $D_H^{ap/melt}$ of 0.25 [22]. Alternatively, water in these minerals may have been in part lost during magma degassing or impact even if nakhlites are the least shocked of all Martian meteorites [17].

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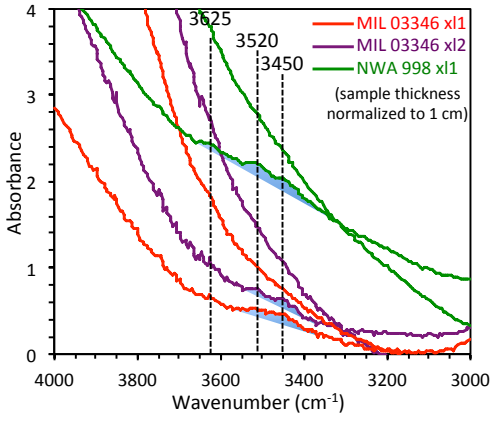
Figure: Transmission polarized FTIR spectra of nakhlite pyroxenes in the O-H vibration region. The fact that the OH bands (in blue) change in position and height with rotation of the infrared polarizer (2 perpendicular directions shown for each pyroxene grain (xl)) demonstrates that they are caused by H defects intrinsic to the pyroxene. 3625, 3520 & 3450 are typical clinopyroxene OH bands.



IDENTIFICATION AND MAPPING OF OLIVINE, ANORTHOSITE AND SNC-LIKE MATERIALS ON MARS: INSIGHTS TO MANTLE RESERVOIRS. F. Poulet[1], A. Ody[1], J. Carter[1,2]. [1]Institut d'Astrophysique Spatiale, Université Paris Sud, 91405 Orsay Cedex, France (francois.poulet@ias.u-psud.fr), [2]European Southern Observatory, Santiago de Chile, Chile.

Introduction: It is presumed that, as on Earth, basaltic magma compositions can form through partial melting of the Martian mantle. Remote-sensing studies including spacecraft observations, can provide insight into the composition and distribution of Mars surface materials, and therefore into the compositional evolution of the mantle and the crust. The intent of this work is to use the CRISM and OMEGA datasets to identify and characterize the spatial distribution of olivine and anorthosite as well as to identify and map areas of possible source regions of basaltic shergottites. Their origin and the implication of their occurrence on the composition of the Martian mantle and crust, as well as on the evolution of Mars volcanism are discussed.

Spatial distribution of olivine The spatial and statistical analysis of the global olivine distribution points out several major geological settings where olivine is detected [1]. Olivine is associated to ancient (early) Noachian crustal rock and to early Hesperian volcanism; by contrast, it is not detected in later Noachian terrains, which cover the major part of the southern highlands. This could reflect a difference in the composition of the parent rocks, with mid- to late Noachian material deriving from olivine-poor bedrock relative to early Noachian and Hesperian units. We also observed numerous early Hesperian olivine-enriched smooth crater floors and flat inter-crater plains throughout the southern highlands. These deposits result from infilling of olivine-rich lava restricted to a limited duration, from 3.8 to 3.6 Ga typically. This significant planetary-scale volcanic activity could correspond to a peak global flux. Finally, olivine is found around the two main basins Argyre and Hellas, with a distribution that takes the form of discontinuous olivine-enriched mixtures exclusively localized on hills associated to Noachian units Nplh and Nh1 that are among the oldest geologic units on Mars. We interpret these olivine-bearing hills as olivine-bearing material excavated from the upper mantle/lower crust during the impact. These observations support mantle overturn.

Identification of anorthositic rocks. Anorthosite is an intrusive igneous rock that exhibits high plagioclase content. On Mars, there are several reasons to explain why such rocks would not have been formed [2]. Based on CRISM instrument, we report the detection of a least 8 distinct anorthosite exposures on Mars mostly associated to excavated and/or uplifted early Noachian materials. Significant quantities of anorthositic rocks can be produced either globally during differentiation through magma-ocean or serial magmatism as for the Moon [e.g. 3,4] or locally requiring mechanisms such as fractional crystallization, assimilation, or partial melting of an already evolved (i.e., not ultramafic) source. The very small number of detections is in better agreement with a localized origin implying partial melting and fractional crystallization of a plutonic source. Of special interest are the presence of altered anorthosite and phyllosilicates. This implies that the anorthosite-bearing rocks were formed before the major period of aqueous alteration, which is consistent with the very ancient age of some deposits.

Sources regions of SNCs. Locating one or more regions with composition similar to that of Martian meteorites would provide key information on the Martian crust and mantle, through the extensive laboratory investigations on these meteorites. In addition, it would enable an absolute age calibration of major Mars events. The study presented here focuses on basaltic shergottites. We have confidentialy identified areas with near-infrared spectral properties similar to those of basaltic shergottites [5]. These regions are found in the Hesperian volcanic provinces of Hesperia Planum, Syrtis Major and Thaumasia Planum. No young analogue mineralogical sites have been found. This could result from the scarce presence of Amazonian volcanic deposits conspicuous in the NIR. An old age (possibly 4.0 Gy [6]) would better explain that ancient crustal rocks are closer to the composition of basaltic shergottites. This is also consistent with a comparison of the OMEGA-based Mars modal mineralogy of martian mafic regions with those of basaltic shergottites [7]. The observed trend in pyroxene ratio, which favors a decrease of the low calcium pyroxene abundance through time, is also difficult to reconciliate with the young age of shergottites.

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METAL-SILICATE PARTITIONING OF SIDEROPHILE ELEMENTS: APPLICATION TO CORE-MANTLE DIFFERENTIATION IN MARS. N. Rai and W. van Westrenen, Faculty of Earth and Life Sciences, VU University Amsterdam, The Netherlands (n.rai@vu.nl).

Introduction: A major outcome of core-mantle differentiation in the terrestrial planets is that the bulk of the siderophile elements are strongly partitioned into the iron-rich metallic core, leaving the silicate mantle and crust relatively depleted in those elements. Since the partitioning of these elements into metallic phases is governed by their metal/ silicate partition coefficients (D) and the pressure-temperature-composition conditions during core formation, the measured or estimated abundances of these elements in a planet's silicate reservoirs can in principle be used to constrain core formation conditions. In the case of Mars, it was previously established that within 13 Ma after accretion, it underwent very fast and large-scale differentiation into a metallic core and silicate mantle [1-3]. Previous studies [4-7] suggest a range of *T* and *P* conditions (1 bar to 14 GPa) for metal-silicate equilibration in a martian magma ocean, at which the measured siderophile element abundances in martian meteorites could have been established. Here we re-examine whether a consistent set of core formation (*P-T-X-fO_2*) conditions can be obtained to match the observed siderophile element depletions in silicate Mars, based on recent advances in our understanding of siderophile element metal-silicate partitioning.

Approach: Geochemical models for the composition of the silicate portion of Mars are mostly based on the composition of SNC (Shergotty-Nakhla-Chassigny) meteorites. These models [5,8,9] suggest that the martian core comprises 20.6 – 23 % of the mass of Mars. We combine recently published metal-silicate partitioning data for Ni, Co, W, Mo, P, Ga, Ge, V, Cr and Mn with literature data [10-21] and characterize the dependence of metal-silicate partition coefficients (D) on temperature, pressure, oxygen fugacity and silicate melt structure and composition to derive equations of the following form:

$$\log D = \alpha + \beta(\Delta IW) + \delta(1/T) + \varepsilon(P/T) + \chi(nbo/t) \quad (1)$$

Trace elements in metal alloys strongly interact with major components such as Fe, Si, C and S, causing metal-silicate partitioning experiments performed under different metal compositional conditions to produce scattered results. Using a thermodynamic approach [15], all metal-silicate partitioning data used in our study were corrected to a common reference point which is the effective value for a trace component mixing in pure metallic iron in the liquid state. All partitioning data were parameterized according to Equation (1). For each element, only statistically valid regression coefficients were considered. Our parametrizations are based on partitioning data obtained at pressures between 6 GPa and 25 GPa, covering the range of pressures in Mars. Using these parameterizations and the proposed bulk Mars composition of [5,7], we assess whether *P-T-X-fO_2* conditions exist that are consistent with single-stage core formation in Mars.

Results: Our initial models assume a predominantly iron rich core. Results indicate that the measured abundances of Ni, Co, W, Mo, Ga, Ge, P and Cr in martian meteorites can be explained by metal-silicate equilibration at conditions of 8 GPa, 2200 K , IW-1.5 and nbo/t~2.55. However, V abundances could not be matched as it remains more lithophile than required under these conditions.

Outlook: The Martian core is much more sulphur-rich than the core of the Earth [5,8,9], with values between 10 and 16 wt% S proposed. The effect of sulphur on metal-silicate partitioning at high pressure is virtually unconstrained. Experimental work is currently in progress, systematically looking at the effect of sulfur on metal-silicate partitioning of these elements at pressures between 2-24 GPa. We will report our results of these experiments, and their effect on Martian core formation models, at the meeting.

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CRYSTALLIZATION OF Y980459 AT 0.5 GPa: ARE RESIDUAL LIQUIDS SIMILAR TO QUE94201?

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Introduction: Y980459 and QUE94201 (denoted Y98 and QUE respectively) are amongst the few martian meteorites thought to represent bona fide liquid compositions [1-4] rather than having formed as a result of crystal accumulation. They represent potential end member compositions for martian basaltic magmas: Y98 is the most mafic of the shergottites [4], and QUE the most evolved [5]. They also share geochemical characteristics that suggest that they sample a similar highly depleted mantle reservoir [6,7].

As examples of liquid compositions, Y98 and QUE hold the most potential for providing information on martian mantle source regions, magma generation and evolution. Although they are of different ages, and therefore not cogenetic, they may reflect the range of petrogenetic processes and evolution for martian basalts, and thus provide some insight into magma production within the martian mantle.

Attempts to determine the relationship between the two types of magmas include petrogenetic models constructed using MELTS [8], which suggest that a Y98 starting liquid can crystallize to a QUE-like assemblage at 1 bar. However, 1 bar experiments have been somewhat unsuccessful at replicating this result [9]. Previous experimental crystallization studies of Y98 by our group [10] at 0.5 GPa have produced melt compositions approaching that of QUE, although these results were complicated by the presence of small, variable amounts of H_2O in some of the runs owing to the use of talc/pyrex experimental assemblies. Therefore we have repeated the four experiments reported by [10], augmented with additional runs, all using $BaCO_3$ cell assemblies, which are devoid of water, and these new experiments supersede those reported earlier. Here we report results of piston-cylinder experiments at 0.5 GPa simulating equilibrium crystallization, and some preliminary fractional crystallization experiments. Equilibrium experiments are carried out using the same bulk composition, whereas fractional experiments are performed using a starting material having the composition of the liquid from the previous experiment.

Results: Equilibrium experiments produce a melt that is similar to the QUE bulk composition in both major and trace elements, although TiO_2 and P_2O_5 are less enriched than in QUE. In contrast, the crystallizing assemblages differ from QUE's near-liquidus assemblage. Olivine is present in all experiments, whereas QUE is olivine-free. Plagioclase is present only in the lowest temperature run, and only in small quantities. Although pyroxene compositions trend towards the ferroan pyroxenes in QUE observed by [5], they are not a good match. Preliminary fractional experiments, on the other hand, produce pyroxenes that match more closely with those in QUE than with those in Y98 (fig. 1), but there is no coexisting plagioclase in this preliminary run, and the melt composition is much more evolved than QUE, with an Mg# of 27.

Implications for the martian mantle and basalt petrogenesis: Although Y98 and QUE appear to sample a similar mantle source region, neither equilibrium nor fractional crystallization seems to derive a QUE-like magma from Y98, despite MELTS models suggesting the contrary. Although the crystal cores in QUE reflect equilibration with a melt of the QUE bulk composition, the sample is a mere 7g and relatively coarse grained, possibly biasing estimates of its bulk composition. Additional fractional experiments are ongoing, and may yet yield a closer match. If the mismatch in preliminary fractional results holds, however, QUE may be the result of a lower degree of melting in the mantle, rather than an anhydrous differentiate of Y98-like melt. Alternatively, since previous experiments containing H_2O yielded a better match, H_2O may play an important role in the evolution of martian magmas.

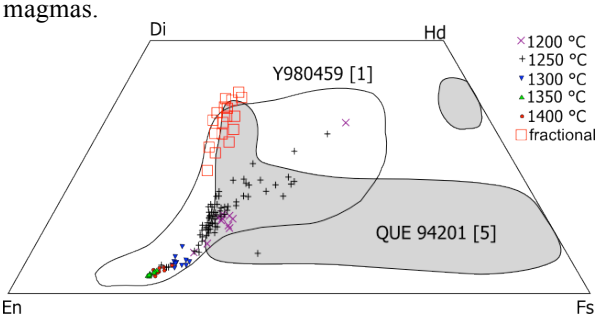

Figure 1: Pyroxene compositions from equilibrium (small symbols) and fractional (large open squares) experiments compared to literature data for pyroxenes in Y98 (outlined) and QUE (gray outline) [1,5]. Equilibrium pyroxenes evolve towards ferrous compositions in QUE but are not a match for QUE. Preliminary fractional experiments appear to produce a better match for QUE pyroxene compositions.

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SIDEROPHILE ELEMENT CONSTRAINTS ON THE CONDITIONS OF CORE FORMATION IN MARS.
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Introduction: Siderophile element concentrations in planetary basalts and mantle samples have been used to estimate conditions of core formation for many years and have included applications to Earth, Moon, Mars and asteroid 4 Vesta [1]. For Earth, we have samples of mantle and a diverse collection of mantle melts which have provided a mature understanding of the how to reconstruct the concentration of siderophile elements in mantle materials, from only concentrations in surficial basalt (e.g., [2]). This approach has led to the consensus views that Earth underwent an early magma ocean stage to pressures of 40-50 GPa (e.g., [3,4]), Moon melted extensively and formed a small (~2 mass %) metallic core [5], and 4 Vesta contains a metallic core that is approximately 18 mass % [6,7]. Based on new data from newly found meteorites, robotic spacecraft, and experimental partitioning studies, [8] showed that eight siderophile elements (Ni, Co, Mo, W, Ga, P, V and Cr) are consistent with equilibration of a 20 mass% S-rich metallic core with the mantle at pressures of 14 +/- 3 GPa. We aim to test this rather simple scenario with additional analyses of meteorites for a wide range of siderophile elements, and application of new experimental data for the volatile siderophile and highly siderophile elements.

New analyses: Analyzes of six shergottites were made using a rastering LA-ICP-MS approach described by [9]. Comparison of our new results to previous analyses of these meteorites shows good agreement, and also includes many additional elements that have not been reported previously.

Mantle concentrations of siderophile elements: We examine Ge-Si, In-Yb, Cu-Ti, W-Ta, Zn-Ti, and Cd-Yb combining our new analyses with previous work (see references in [9]) – all siderophile elements paired with lithophile elements of similar compatibility in igneous fractionation processes. For Ge, terrestrial peridotite and basalt define a very clear line in correlation with Si, and therefore the slightly lower concentrations of Ge in martian basalt result in the martian mantle estimate just below the terrestrial trend (see [9]). Cu shows a significantly larger depletion relative to the terrestrial peridotite and basalt. Our new W data help better define the W depletion derived by [8]. New Zn and In data indicate little to no depletion in the martian mantle, and Cd is depleted more in the martian mantle than in the terrestrial mantle.

Implications: All of these new mantle concentration estimates, combined with partitioning studies, are used to test the concept of a 14 GPa early martian magma ocean. The moderately siderophile elements (W, Mo) are consistent with this idea, even with revised depletions and significant new experimental data. The volatile siderophile elements Ge, In, Cu, Zn and the highly siderophile elements Au and Pd (and possibly Pt and Ir) are all consistent with a 14 GPa magma ocean (see Ge in Figure 1). This suggests Mars experienced continuous growth of a metallic core, and did not require changing redox conditions or a late chondritic additions to explain these elements, as argued for Earth (e.g. [4]). In addition, the magma ocean scenario is supported by lithophile isotopic systems Nd and Hf [10].

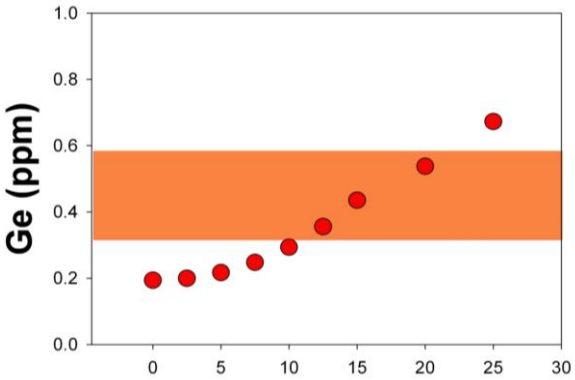

Figure 1: Calculated Ge content of the martian mantle, as pressure increases along a magma ocean adiabatic gradient during growth of Mars. Horizontal band is the estimated range of Ge contents from the Ge-Si correlations from [8]. The calculated mantle Ge contents during growth of Mars coincide with the horizontal band between 12 and 20 GPa, and thus are consistent with a magma ocean scenario like that proposed by [8].

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REDOX SYSTEMATICS OF MARTIAN MAGMAS WITH IMPLICATIONS FOR MAGNETITE STABILITY. K. Righter[1], L. Danielson[2], K. Pando[2], R.V. Morris[1], T. G. Graff[2], D. G. Agresti[3], A.M. Martin[1], S. Sutton[4,5], M. Newville[5], A. Lanzirotti[5], [1]NASA/JSC, [2]ESCG, Houston, TX 77058, [3]University of Alabama at Birmingham, [4]Department of Geophysical Sciences and [5]Center for Advanced Radiation Sources, Univ. Chicago.

Introduction: Iron redox systematics of the high FeO shergottitic liquids are poorly known, yet have a fundamental control on stability of phases such as magnetite, ilmenite, and pyroxenes [1].

Experiments: We undertook experiments to constrain the $Fe^{3+}/Fe(tot)$ in high FeO glasses as a function of fO_2, melt P_2O_5, temperature and pressure. We also performed a series of sub-liquidus experiment between 1100 and 1000 °C and FMQ+0.5 to FMQ-1 to define magnetite stability. Experiments were performed at JSC in either the 1 bar gas mixing lab, or in a piston cylinder or multi-anvil presses in the high pressure experimental petrology lab.

Analyses: Run products were analyzed for Fe^{3+} and Fe^{2+} by either Mössbauer spectroscopy [2] or micro-XANES (x-ray absorption near edge structure) spectroscopy [3].

Results: One bar glasses equilibrated at FMQ-3 to FMQ+3 show a much lower $Fe^{3+}/Fe(tot)$ than terrestrial basalts at the same conditions (Figure 1). As melt P_2O_5 contents increase from 0 to 3 wt% (at fixed pressure, temperature and fO_2), $Fe^{3+}/Fe(tot)$ decreases from 0.07 to 0.05. Temperature increases between 1200 and 1500 °C cause little to no variation in $Fe^{3+}/Fe(tot)$. Pressure increases from 1 to 4 GPa cause a slight decrease in $Fe^{3+}/Fe(tot)$. The trends with pressure and temperature are in agreement with results of previous studies on terrestrial compositions [4-6].

Implications: Combining our new series of data allows derivation of an expression to calculate $Fe^{3+}/Fe(tot)$ for high FeO melts such as martian magmas.

$$\ln(Fe^{3+}/Fe^{2+}) = = a\ \ln fO_2 + b/T + cP/T + dXFeO + eXAl_2O_3 + fXCaO + gXNa_2O + hXK_2O + iXP_2O_5$$

This expression can be used to show that decompressed melts become slightly more oxidized at the surface (compared to 4 GPa).

Magnetite stability is suppressed by the lower $Fe^{3+}/Fe(tot)$ of the high FeO melts. Magnetite stability is a function of Fe_2O_3 and temperature and is stable ~50 °C lower than typical terrestrial basalt (Figure 2). Difficulty in producing magnetite as a liquidus phase in magmatic systems suggests either that many martian basalts are more oxidized, that the titano-magnetite only forms upon cooling below ~ 1000 °C at FMQ, or that the magnetite has a secondary origin.

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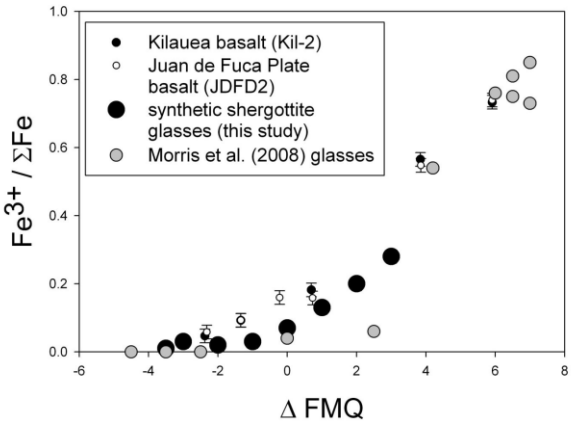

Figure 1: New results for glasses measured using Mössbauer spectroscopy illustrating that the shergottite composition remains low relative to terrestrial basalts such as mid ocean ridge (JDFD2) and Hawaiian (Kil-2) basalts (from [4]).

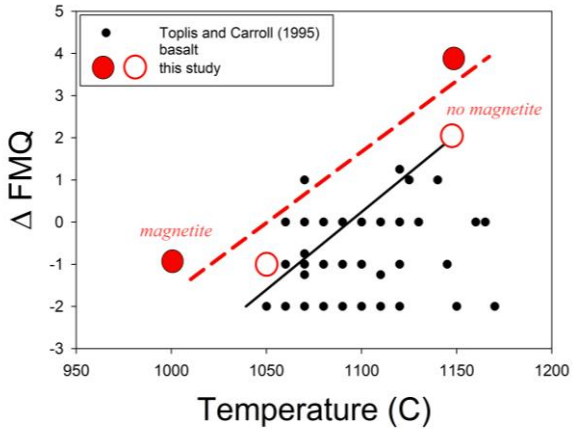

Figure 2: Comparison of magnetite saturation conditions (T and fO_2) for a terrestrial ferrobasalt [7] and a martian shergottite (this study and [8]). High FeO shergottite melts (dashed line) saturate magnetite about 50 °C lower than terrestrial basalt (solid line).

Coupled Core Cooling and Mantle Dynamics on Mars. J. H. Roberts[1] and J. Arkani-Hamed[2], [1]Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723 (James.Roberts@jhuapl.edu), [2]Department of Physics, University of Toronto, Toronto, ON, Canada M5S 1A7.

Introduction: Over twenty mid-Noachian basins with diameters over 1000 km have been identified on Mars [1]. Heating by such impacts may have suppressed core cooling [2,3], contributing to the cessation of dynamo activity [4], as well as modifying the pattern of mantle convection [5]. Here we investigate the thermal evolution of Mars in response to the largest basin-forming impacts, using coupled models of mantle convection and parameterized core cooling.

Coupled core and mantle dyanmics: The chief difficulty in full coupling of 3D mantle convection models to core dynamo models is that relevant timescales are quite different. Most studies therefore are of either the core *or* the mantle, and treat the other layer as a boundary condition. Here, we are interested in heating by large impacts which instantaneously change the temperature structure in the core and mantle.

We model convection in the mantle using the finite element code Citcom in 2D axisymmetric geometry, appropriate for a single impact scenario. At the time of an impact we introduce a temperature perturbation resulting from shock heating into the core and mantle layers (see Figure 1a). Because lateral mixing of the core occurs very quickly compared to mantle dynamics, we assume the core becomes stratified [3] and its temperature varies only radially.

We fix the mantle temperature and solve the 1D enthalpy equation in the core and lower thermal boundary layer of the mantle. After a time corresponding to a mantle timestep, we update the temperature at the CMB and mantle boundary layer, and let the mantle convection progress for one timestep. We continue this iteration until the core temperature becomes almost adiabatic and the entire core is convecting. Mantle convection then proceeds while the entire core cools retaining an adiabatic temperature distribution.

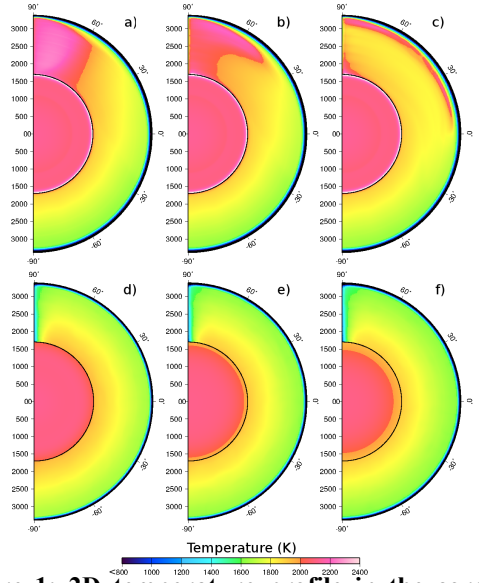

Figure 1: 2D temperature profile in the core and mantle immediately after the impact at the top of the figure (a), and after 14 ky (b), 214 ky (c), 164 My (d), 387 My (e), and 642 My (f). CMB is marked by a black line.

Results and Discussion: Preliminary models have been performed in 2D to speed computation times. We have imposed the heating due to a 1000 km diameter rocky projectile impacting Mars at 10 km/s. Figure 1 shows that the impact heating generates a strong hemispheric pattern of mantle convection which quickly spreads into a warm layer beneath the stagnant lid, and decays. Figure 2 shows the evolution of the core temperature profile following the impact. While the thermal "blanket" in the outermost core disappears quickly, the core does not return to a fully convective state for ~ 0.5 Gy following the impact.

Our results suggest that a pre-exisitng core dynamo would have been crippled for at least a similar timescale. Theoretically, the dynamo could restart once core temperature became adiabatic. However, so much time, there may be insufficient CMB heat flow to restart dynamo activity, particularly if the pre-impact dynamo was subcritical [5].

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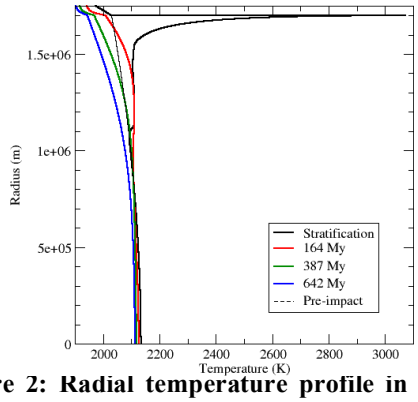

Figure 2: Radial temperature profile in the core and lower mantle following the impact heating. Red, green and blue curves correspond to panels d-f in Figure 1.

THERMAL AND COMPOSITIONAL EVOLUTION OF THE MARTIAN MANTLE. Thomas Ruedas[1], Paul J. Tackley[2], and Sean C. Solomon[1], [1]Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, D.C., USA, [2]Institut für Geophysik, ETH Zürich, Switzerland.

Introduction: We present new numerical models for the thermochemical evolution of the mantle of Mars over the past 4 Gy. Among other questions, we examine if a perovskite+ferropericlase layer exists at the base of the martian mantle, if long-lived plumes can explain the volcanic provinces, under which circumstances Mars may still be volcanically active, and the iron and radionuclide abundances of the martian mantle. Specifically, we have developed a parameterized model of composition and thermoelastic properties of mantle material and combined it with the two-dimensional, anelastic, compressible convection and melting algorithm of STAGYY [1,2] in a spherical annulus geometry [3]. These models include a detailed treatment of the effects of solid–solid phase transitions and of compositional changes that accompany generation and removal of mantle partial melt during magmatism, especially the redistribution of radionuclides and, in a subset of the models, water. The thermal evolution of the core is included as a parameterized one-dimensional model after Nimmo et al. [4].

Results: The results of the models are compared with geophysical and chemical observations from spacecraft and information from martian meteorites (Fig. 1). Most models yield crustal thicknesses between ~75 and 90 km, ancient depths for the Curie temperatures of candidate magnetic minerals that include the entire crust, and mechanical lithosphere thicknesses that increased from less than 100 km in the Noachian to ~200–250 km now. Generally, models with a large core, Mg#=0.75, and radionuclide contents based on those suggested by [5] tend to explain observations best; an example is shown in Figure 2. However, only a subset of the models develops a pattern of mantle convection that evolves towards two or three large, long-lived plumes, and it takes at least ~2 Gy before this stage is reached. Moreover, the temporal stability of plumes decreases strongly if the influence of water on mantle viscosity is included, and models with a very low-viscosity deep mantle barely develop whole-mantle plumes at all. As Tharsis and probably Elysium are older than 2.5–3 Gy, model assumptions more complex than those made in this study are required to explain these major volcanic provinces.

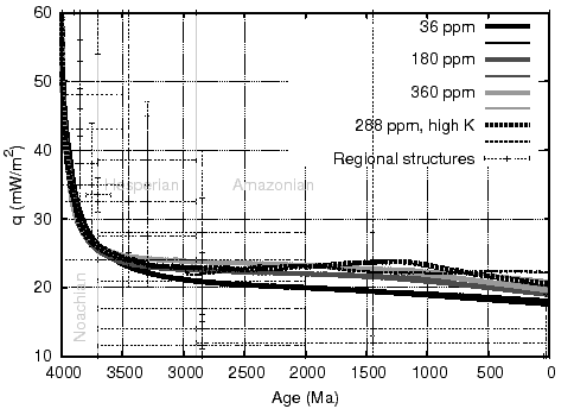

Figure 1: Average surface heat flux for models with varying mantle water concentrations (given in ppm). ^{40}K in the "high K" model is 3 times higher than in [5]. Regional heat fluxes are from various studies (e.g., [6]).

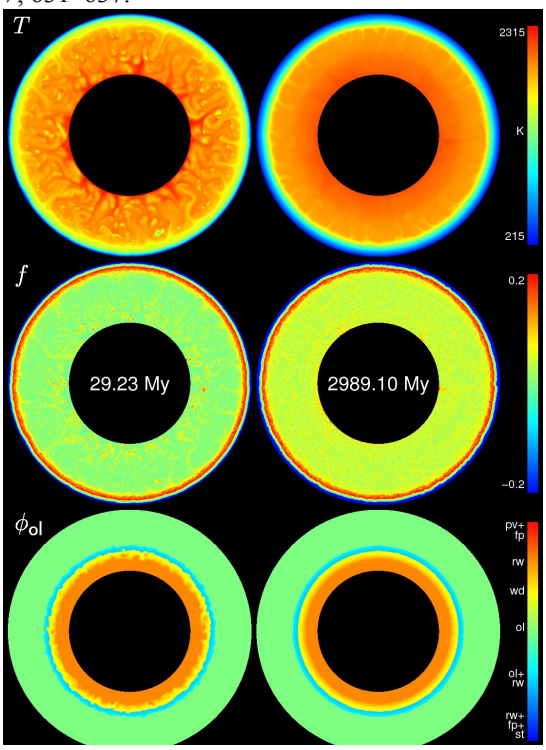

Figure 2: Two snapshots of the temperature, melting degree, and $(Mg,Fe)_2SiO_4$ phase fields of a water-free model with a large core (r_c=1690 km) and an initial potential mantle temperature of 1873 K.

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Exploring the martian mantle through the micro-scale examination of the geochemical, fO_2, and kinetic crystallization history of olivine in shergottites. C.K. Shearer[1], P. Aaron[1], P.V. Burger[1], A. Bell[1], Y. Guan[2], and J.J. Papike[1]. [1]Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131. [2]Division of Earth and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

Introduction: A striking geochemical feature of the shergottites is the large range in initial Sr isotopic ratios and initial ε^{Nd} values [i.e. 1-4]. Within this range, the shergottites do not form a radiogenic isotopic continuum, but instead fall into three discreet subgroups. Each subgroup has distinct geochemical characteristics (i.e. bulk rock and phosphate REE patterns, stable isotopes, fO_2)[4-8]. These characteristics have been linked to different reservoirs in the martian mantle and crust and their interactions during shergottite magmatism. Two end-member models have been suggested to account for these ranges in geochemical characteristics. In one model, the shergottites are products of melting of two distinctly different mantle sources; a reduced (<IW+1), depleted mantle and an oxidized (~IW+3.5), enriched mantle. The second model suggests that shergottites that are reduced-depleted reflect the martian mantle, whereas the more oxidized and enriched shergottites reflect interactions between mantle-derived basalts and the martian crust [4-8]. Using high beam current electron microprobe x-ray mapping, nano-SIMS trace element analyses (including multi-valent trace elements such as V), and XANES analyses of V valance state, we are reconstructing the geochemical, fO_2, and kinetic crystallization history of olivine megacrysts in depleted (i.e. Y980459) and enriched (i.e. NWA1183) shergottites. This reconstruction will allow us to determine the origin of these megacrysts and provide additional insight into the martian mantle.

Previous interpretations of olivine megacrysts: Numerous studies [i.e. 8-10] have determined that megacryst cores from depleted shergottite Y98 are in chemical equilibrium with the Y98 whole-rock composition based on exchange K_D^{Fe-Mg} between olivine and the bulk rock. Therefore, they concluded that these megacrysts are phenocrystic in origin and that the mantle source for Y98 was at an fO_2 of IW+1. Usui et al. [10] argued that the olivine megacrysts in Y98 crystallized at slightly more reducing conditions than the groundmass olivine. On the other hand, Herd [11] observed that in NWA 1086/1110 (=NWA1183) the earliest phases (i.e. chromite, olivine cores) crystallized at an fO_2 of IW+1, whereas late-stage phases (i.e. titanian-spinel rims, olivine rims) crystallized at far more oxidizing conditions (i.e. QFM + 0.3). Herd [11] concluded that the fO_2 calculations and textural observations are indicative of a xenocrystic origin for the olivine megacrysts and that this supports a model in which martian basalt fO_2 is determined by mantle-source redox conditions.

Observations and interpretations: Our observations reveal a more complex crystallization history for both basalts. As shown in Fig. 1, whereas the Fe x-ray map indicates a simple crystallization history for Y98, the P map illustrates a P-rich reabsorbed core surrounded by oscillatory P zoning. Vanadium is not correlated to P-enrichments. There may be a slight increase in fO_2 from the absorbed core to the rim [10]. Conversely, NWA1183 does not exhibit any textural features that indicate absorption of xenocrystic olivine. Rather, it exhibits a euhedral core surrounded by oscillatory P zoning. In this case, V is correlated to P. The difference in the behavior in V between Y98 and NWA

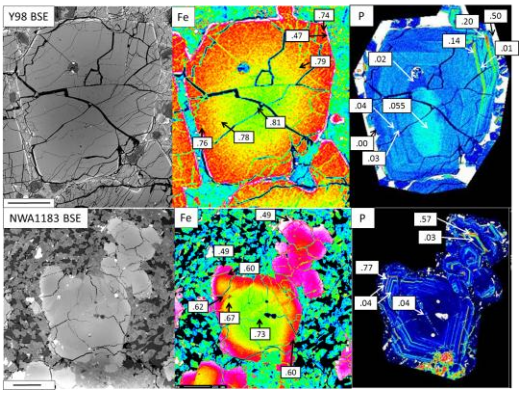

Fig. 1. BSE, Fe, P x-ray maps of olivine in Y98 and NWA1183. Values in Fe maps are Mg# and wt.% P_2O_5 in P maps.

1183 can be attributed to differences in fO_2 which influences the valence state of V (V^{3+} in Y98; $V^{4+,5+}$ in NWA 1183) and the nature of V substitution into olivine. This suggests that during the formation of the oscillatory zoning in NWA1183, the fO_2 was perhaps near the conditions suggested by [11]. Olivines in both basalts record a process of oxidation during crystallization. The increased oxidation is more pronounced in NWA1183. One interpretation is that suggested above by Herd [11]. Alternatively, the changing fO_2 could be a product of auto-oxidation during degasing of Cl-bearing aqueous volatiles[12]. One implication of the latter interpretation is that the source regions for all shergottites are at an fO_2 more reducing than IW+1.

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Carbon/carbonate equilibria within a Fe-rich mantle peridotite. V. S. Stagno[1], D. J. Frost[2] and Y. Fei[1], [1]Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA (vstagno@ciw.edu), [2]Bayerisches Geoinstitut, Universität Bayreuth, D-95440, Germany.

Introduction: The speciation of volatiles in the C-O-H system within a silicate mantle likely depends on the oxygen fugacity buffered by heterogeneous equilibria involving mineral phases with variable Mg/Fe ratios. At reduced conditions carbon will be stable instead of carbonate, and this will limit the mobility and reactivity of carbon. In the Earth's interior the fo_2 at which carbon coexists with carbonate within peridotites is defined by equilibrium involving silicates, such as olivine and opx (EMOD buffer). Such phases are sensitive to melting processes as consequence of their Mg/Fe partitioning with the coexisting melt. In this study we performed experiments at the aim to test the applicability of the EMOD buffer to more Fe-rich compositions. We also measured the Mg/Fe partitioning between silicate and liquids as function of the oxygen fugacity.

Experimental technique: We performed experimental measurements of the oxygen fugacity at which carbon and carbonate (solid or liquid) coexist within a peridotite assemblage in the system Ca-Mg-Fe-Si-O-C. Experiments were performed between 3 and 6 GPa and 800-1500 °C using multi anvil apparatus. The starting material was representative of the *enstatite + magnesite = olivine + carbon +* O_2 equilibrium (EMOD buffer) [1] and prepared using a mineral mixture of synthetic (or natural) olivine, opx, cpx, graphite and magnesite loaded into a graphite capsule, then wrapped by rhenium foil. We performed experiments at different iron contents using synthetic olivine with different Mg/(Mg+Fe) ratio. The oxygen fugacity was calculated using Ir metal as a redox sensor [1, 2]. Chemical compositions of the recovered run products were obtained by electron microprobe.

Results and conclusions: Preliminary results at 3 and 6 GPa show the occurrence of carbonate-silicate melts coexisting with olivine, opx and cpx characterized by high iron content at temperature well below the solidus of a carbonated peridotite with a BSE composition. First measurements of the fo_2 using the Ir sensor show that the carbon/carbonate equilibrium falls at least 2 log units below the EMOG/D buffer at the same temperature and pressure than in a peridotite. Further, we observed that carbonate melts in equilibrium with mantle-like olivine show high values of K_D, which implies small Fe contents until a Fe# in olivine of 0.12 beyond which the K_D suddenly decreases as a consequence of increasing Fe content in melts.

Results from this study will help to improve our knowledge on the effect of bulk chemistry on carbon bearing redox reactions and possible implications for the dissolution of carbonate in liquids equilibrated with a Mars-like mantle composition at low fo_2.

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HEAT CAPACITY OF MARS. M. Szurgot, Technical University of Lodz, Center of Mathematics and Physics, Al. Politechniki 11, 90 924 Lodz, Poland, (mszurgot@p.lodz.pl).

Introduction: Relationships between thermophysical properties and bulk density of meteorites have beeen recently established [1-3], and applied for evaluation of heat capacity of extraterrestrial objects [4]. Heat capacity C of Mars, Martian mantle, crust and core can be determined using the equation

$$C = M \cdot Cp, \quad (1)$$

where M is the mass, and Cp is specific heat capacity. Cp can be determined using the relationship between Cp (J/(kg·K) and bulk density d (kg/m^3) of meteorites

$$Cp = a + b/d, \quad (2)$$

where a, and b are constants (a = 303 J/(kg·K), b = 1.31· 10^6 J/K·m^3) [1]. Equation (2) satisfactorily describes Cp(d) dependence at room temperature. Our recent results show that heat capacity of terrestrial planets is in the range of 10^{26} - 10^{27} J/K, asteroids 10^{14} - 10^{23} J/K, and of natural satellites 10^{18} - 10^{26} J/K at room temperature [4].

Cp(T) dependence needs inserting a correction factor into eqs. (1) and (2) (factor f). Since temperature of Martian core and mantle is high (1200 -1600 K for mantle [5], and 1771-1950 K [5, 6-9] for core), one has f > 1. An analysis of literature data on Cp(T) dependence for mantle and core materials shows that Cp is about 1.6-1.7 times higher at high temperatures than at room temperature (e.g [10]). As a result, value of f*mantle* = 1.6 is chosen for the Martian mantle, f*Mars* = 1.6 for the global Mars, and value of f*core* = 1.7 for the core. For the Martian crust f*crust* ≈ 1 since the average temperature of crust 310 K, estimated as mean of 210 and 411 K [5], is close to room temperature.

The aim of the paper was to estimate heat capacity of the Martian mantle, core and crust, and the global heat capacity of Mars.

Results and discussion: Table 1 presents results of calculations of Cp and C values for the crust, mantle, and core of Mars, and the whole Mars planet. The data show that specific heat capacity Cp of mantle material at high temperatures is 1080 J/(kg·K), the core material is 831 J/(kg·K), and the whole Mars is 1016 J/(kg·K). High-temperature value of heat capacity C of Mars is equal to 6.52·10^{26} J/K, mantle is equal to 5.2·10^{26} J/K, and core 1.16·10^{26} J/K.

Table 1 reveals that dominant contribution to the global heat capacity of Mars comes from the mantle (*Cmantle*/C*Mars* ≈ 0.80), the second contributor is core (*Ccore*/C*Mars* ≈ 0.18), and the crust contribution is small ((*Ccrust*/C*Mars* ≈ 0.02). The sum of crust, mantle and core contribution gives the same global heat capacity (C*Mars* = 6.52·10^{26} J/K) as it was calculated directly using the mean density of Mars. It proves that the values of mass and mean densities of crust, mantle and core [6,7], used in these calculations, are correct.

Table 1 Heat capacities of crust, mantle and core of Mars, and the global heat capacity of Mars.

	M(kg)	d(g/cm^3)	Cp(J/(kg·K))	C(J/K)
Crust	0.22·10^{23}	2.99	741	0.16·10^{26}
Mantle	4.81·10^{23}	3.52	1080	5.20·10^{26}
Core	1.39·10^{23}	7.04	831	1.16·10^{26}
Mars	6.42·10^{23}	3.94	1016	6.52·10^{26}

Table 1 shows that heat capacity C increases with increasing mass M. Dependence of C on mass of Martian components and Mars is linear, and C(M) function can be expressed by the equation

$$C = A \cdot M + B, \quad (3)$$

where A, and B are constant. Constant A is the slope of the straight, and B is the intersept (A= (1061 ± 48) J/(kg·K; B = (-0.147 ± 0.194)·10^{26}J/K; R^2=0.998). Constant A represents the mean specific heat capacity, and is close to the silicate material of mantle (1080 J/(kg·K)).

It is seen that the dominant contributor to the mass of Mars (75%) determines both the global heat capacity of Mars and the mean specific heat capacity of Mars.

Conclusions: The specific heat capacity of Mars' mantle is 1080 J/(kg·K), and heat capacity of mantle is 5.2·10^{26} J/K. The mantle is the main contributor to the mean value of specific heat capacitiy of Mars (1016 J/(kg·K), and to the global heat capacity of Mars (6.52·10^{26} J/K). Heat capacity is a linear function of mass of Martian components.

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THE COMPOSITION OF BULK SILICATE MARS. G. Jeffrey Taylor, Hawaii Institute of Geophysics and Planetology, SOEST, University of Hawai'i, Honolulu, HI 96822; gjtaylor@higp.hawaii.edu

Introduction: Data from the Mars Odyssey orbiting gamma-ray spectrometer (GRS), Pathfinder and MER rover missions, and the growing collection of SNC meteorites allow us to test models of the bulk composition of Mars. The most robust of these models is that of Wänke and Dreibus (W-D) [e.g., 1], which is based on the compositions of SNC meteorites. I focus here on bulk silicate Mars. Determining planetary bulk compositions is crucial to understanding accretion, differentiation, and crust-mantle evolution. For example, knowing the bulk composition in principle allows us to understand the formation of the distinctive source regions (e.g., enriched and depleted shergottites) of SNC meteorites. These processes, of course, make it tricky to extract the bulk composition from geochemical and geophysical data.

FeO: It is certain that Mars is richer in oxidized iron than is Earth. SNC meteorites contain on average 19.5 wt% FeO (my compilation of published data); GRS data give a global mean of 18.4 wt% [2]; and average surface soils at the landing sites is 19.2 wt% [3]. GRS data vary regionally, but FeO concentrations are everywhere greater than in terrestrial MORB samples (~10 wt%). A straightforward, though not particularly elegant way to determine FeO in bulk Mars is to assume that the mantle contains about the same amount of FeO as do magmas derived from it (D_{FeO} for major minerals is close to 1), giving bulk composition of 18.4 wt% (using the global GRS data). Slightly more elegant is to use the ratio of the bulk terrestrial FeO of (8 wt%) to the average normal MORBs (10.5 wt%), to estimate a bulk distribution coefficient; this approach gives 15 wt% for bulk Mars. This value is consistent with FeO derived from the Martian moment of inertia [4] and from experimental data [5]. The W-D FeO estimate uses the observation that MnO in SNC meteorites is similar to that of CI chondrites, and then uses the FeO/MnO ratio in SNC meteorites (39.1; additional data gives 40.3) to that in carbonaceous chondrites, giving a bulk Mars FeO of 17.9.

Moderately Volatile Elements: The best way to assess bulk volatile abundances is to examine the ratio of an incompatible volatile (e.g., K) to an incompatible refractory element (e.g., Th). GRS data indicate a global average K/Th of 6000 ± 200 [2, but updated with new spectral analysis]; SNC meteorites range in K/Th from 3100 to 6800. Wänke and Dreibus used K/La in SNC meteorites and assumed chondritic levels of refractory elements to determine a bulk Mars K content of 305 ppm (K/Th of 5450). In spite of the small difference in K/Th, there is little reason to change this estimate of the K concentration in bulk Mars. Concentrations of other elements with similar condensation temperatures and geochemical behavior (e.g., Rb, Cs) follow from their abundances relative to K. Assuming bulk Mars K (305 ppm) and Th (.056 ppm) and that the surface composition applies to the entire crust Taylor et al. [2] estimate that about 50% of the K and Th in bulk Mars is in the crust.

Highly Volatile elements and H_2O: Taylor et al [6] noted that the surface sampled by GRS had on average chondritic K/Cl and given similar condensation temperatures for K and Cl, concluded that bulk Mars contains 390 ppm Cl. This is ten times higher than the W-D value (38 ppm), which was based on Cl contents in SNC meteorites. We [6] suggested that the meteorites, mostly extrusive rocks, lost Cl upon eruption. Data suggest that lava can lose 50% to 90% of its Cl, but the extent of loss depends on eruption details. Because Cl and K are both incompatible elements, half of the Cl is in the crust. If Cl is only 38 ppm in primitive Mars, the high surface concentration implies a substantial concentration of Cl in the uppermost crust. Cl/Br is chondritic in SNC meteorites and surface soils [3], so Br is between 0.145 ppm in bulk Mars (W-D) and 2.2 ppm [6]. Using ratios of incompatible elements to K and all published data for SNC meteorites, we find that other highly volatile elements are similar to the W-D values (in ppb): Tl (4), Bi (0.5), and In (12). Br is likely to be similar in abundance to these elements and given the chondritic Cl/Br ratio, Cl is probably at the W-D value in bulk Mars, implying that the Cl condensation temperature is much lower than calculations suggest. Studies of meteorites indicate that mantle H_2O is 100–300 ppm [e.g., 7]. Since H_2O behaves incompatibly like K, half of is in the crust. Thus bulk H_2O is 200–600 ppm in Mars. GRS data indicate a surface average of about 3.5 wt%, suggesting a strong enrichment of H_2O (or OH) near the surface.

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THE REDOX STATE OF THE MARS MANTLE AS INFERRED FROM MARTIAN METEORITES: RELATIONSHIP TO VOLATILE CONTENT AND OTHER GEOCHEMICAL PARAMETERS. M. Wadhwa[1], [1]Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287 (email: wadhwa@asu.edu).

Introduction: The redox state of the Mars mantle is an important parameter affecting the compositions of magmas and volatile species derived from it. Moreover, it also influences the nature of metasomatic fluids involved in mantle processes and the evolution of the atmospheric composition through time. Although the redox state of the martian interior may be inferred from some of the chemical signatures in surface materials on Mars observed by orbital and landed spacecraft, the most reliable means of determining it is through detailed laboratory investigations of martian rocks that formed by crystallization of magmas derived from the martian mantle.

The more than ~50 or so known martian meteorites currently represent the only magmatic rocks from Mars that are available for studies in Earth-based laboratories. Detailed investigations of these samples can provide constraints on the formation and evolution of the interior and surface of Mars that are complementary to those provided by spacecraft data [1]. In recent years, several investigations of these martian meteorites have provided constraints on fO_2 conditions prevalent during the crystallization of their parent magmas (e.g., [2-9]). Based on such studies, the redox state of the martian mantle from which these magmas originated may be estimated.

Estimation of the redox state of the Mars mantle: A number of different oxybarometers, mostly based on ferrous-ferric mineral equilibria or multivalent minor or trace elements, have been applied to various martian meteorites (but particularly to the basaltic shergottites) (e.g., [2-8]). These different oxybarometers record the redox conditions at different stages during the petrogenesis of a particular sample. As a case in point, it was demonstrated using multiple oxybarometers that redox conditions during the crystallization of the LAR 06319 olivine-phyric shergottite evolved from initial crystallization of the olivine megacrysts at FMQ-2 to later crystallization of the groundmass at close to ~FMQ [8].

As such, different oxybarometers can provide valuable insights into magmatic processes (such as crystallization in a closed versus open system, and degassing of volatiles from the magma etc.) or even post-crystallization secondary alteration (if the oxybarometer is prone to resetting by such processes). However, to obtain the most reliable estimate of the redox state of the mantle source reservoir from which a magmatic sample was derived, it is essential to apply an oxybarometer that is based on the earliest-formed phases and is not easily reset by post-crystallization processes. Furthermore, comparison of redox conditions in the source reservoirs of different martian meteorites should be based on application of the same oxybarometer to these meteorites. The pyroxene Eu oxybarometer meets these criteria, and has been applied to various martian meteorites [2,6,9] that range in age from <200 Ma to ~4 Ga [1]. Based on the application of this oxybarometer, it is inferred that the martian mantle records significant variations in its redox state (from ~3 log units below FMQ to close to ~FMQ). The low end of this scale may reflect the original redox state of the martian mantle following the early global differentiation of Mars. The higher redox state of other martian silicate reservoirs (recorded in the enriched shergottites and the nakhlites) could be due to evolution during the original crystallization of a magma ocean [8], or due to later metasomatism by oxidizing fluids [9], or both.

Relationship to other geochemical parameters: The redox conditions recorded by the basaltic shergottites in particular appear to be related to the degree of incompatible element enrichment (e.g., chondrite-normalized La/Yb ratios in their inferred parent melts), as well as other parameters such as their initial $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios [2-4]. These relationships are best explained in terms of mixing of end-member silicate reservoirs in the martian mantle and/or crust (i.e., in the case of the enriched end-member), although it seems more likely that both depleted and enriched reservoirs reside in the mantle and were established during an early silicate differentiation event on Mars [10]. The redox state of martian mantle reservoirs and their volatile contents (particularly, water) may also be correlated [1,4]. However, a recent study indicates that the water contents of the depleted and enriched basaltic shergottite magmas were similar, and suggests that significant water could be stored in the martian mantle despite the prevailing low redox condition during its original differentiation [11].

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